CHAPTER 4

TREATMENT TECHNOLOGIES

4-1. Applicability. This chapter provides descriptive information on state-of-the-art design methodology for the treatment of industrial and hazardous waste. The information presented is applicable for the planning level design of remedial action treatment systems. The process designs described must be adjusted for site-specific conditions to ensure appropriate technology application.

4-2. Techniques. Because hazardous waste treatment must consider so many materials and conditions, good reliable treatability data are essential. Considerable information is available in the literature that can be used in planning level designs and should be extracted and compiled under one cover. However, final designs must be based upon field data ascertained from bench and/or pilot plant scale testing of specific waste streams. EPA Guidance Manual Guide for Conducting Treatability Studies under CERCLA gives an excellent coverage of this area.

Section I. Treatment of Liquid Waste Streams

4-3. Definitions. Liquid waste streams include leachates, ground water, surface water, concentrated hazardous wastes, and effluents resulting from other treatment technologies such as incineration or soil washing. The technologies presented in this section are commonly used for the treatment of liquid waste streams.

4-4. Air Stripping. Air stripping removes volatile contaminants from an aqueous waste stream by passing air through the wastes. This process can be accomplished either in a stripping lagoon or in a packed column. When air is passed through the waste the volatile dissolved gases are transferred to the air streams for possible collection and treatment in the case of a packed column, if the air stream is considered hazardous. Figures 4-1 and 4-2 illustrate both processes. The major factors affecting performance and design include pH, temperature, Henry*s law constant of the chemicals to be stripped, airflow, hydraulic loading, and column packing depth and spacing. The process requires a high pH, 10.8 to 11.5 for ammonia stripping, and increased airflow as the temperature of the influent stream decreases.

a. Applications. Air and steam stripping have been used to remove volatile organic compounds (phenol, vinyl chloride, etc.) and compounds with relatively high vapor pressure and low solubility such as chlorinated hydrocarbons from waste streams. Air stripping has been directly applied to ground-water treatment in removing trichloroethylene (TCE), trihalomethane (THM), and hydrogen sulfide. Removal rates as high as 99 percent for TCE from ground water have been seen. Air stripping has been widely used to remove ammonia from wastewaters with removal efficiencies exceeding 90 percent.

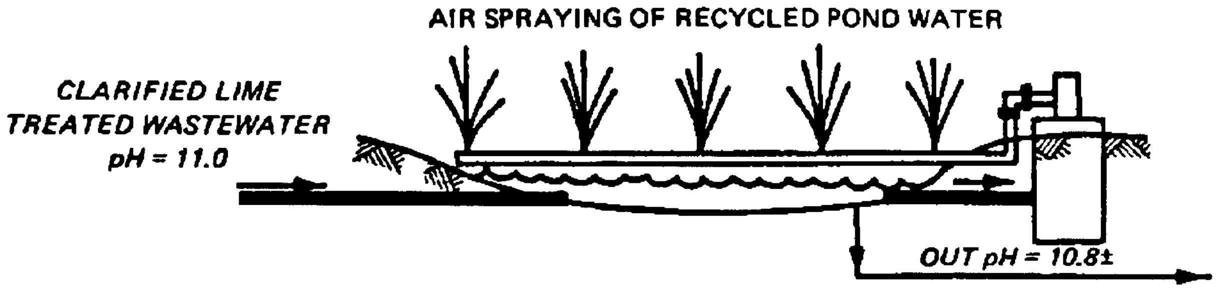


Figure 4-1. Ammonia Stripping Lagoon (Source: EPA 1978)

b. Advantages/Disadvantages. The advantages and disadvantages of air stripping are summarized below.

Advantages	Disadvantages
Can reduce levels of volatiles by over 90 percent	Cost prohibitive to operate at temperatures below freezing
Process is relatively independent of volatile concentration	Sensitive to pH, temperature, and fluxes in hydraulic load
Can reduce TCE concentrations by 99 percent	May pose potential air pollution problems requiring permitting, recovery, and treatment if hazardous volatile organic compounds are present in waste stream

c. Data Requirements. An air stripping system requires the following data.

(1) Feed stream characteristics.

(a) Average water flow, Q, m^3d (mgd).

(b) Peak water flow, m^3d (mgd).

(c) Water temperature, T, °C (°F).

(d) Contaminant concentration in water, Xo, mg/ℓ

(e) pH of water.

(2) Effluent stream characteristics (contaminant concentration, X, mg/ℓ).

(3) Design decisions.

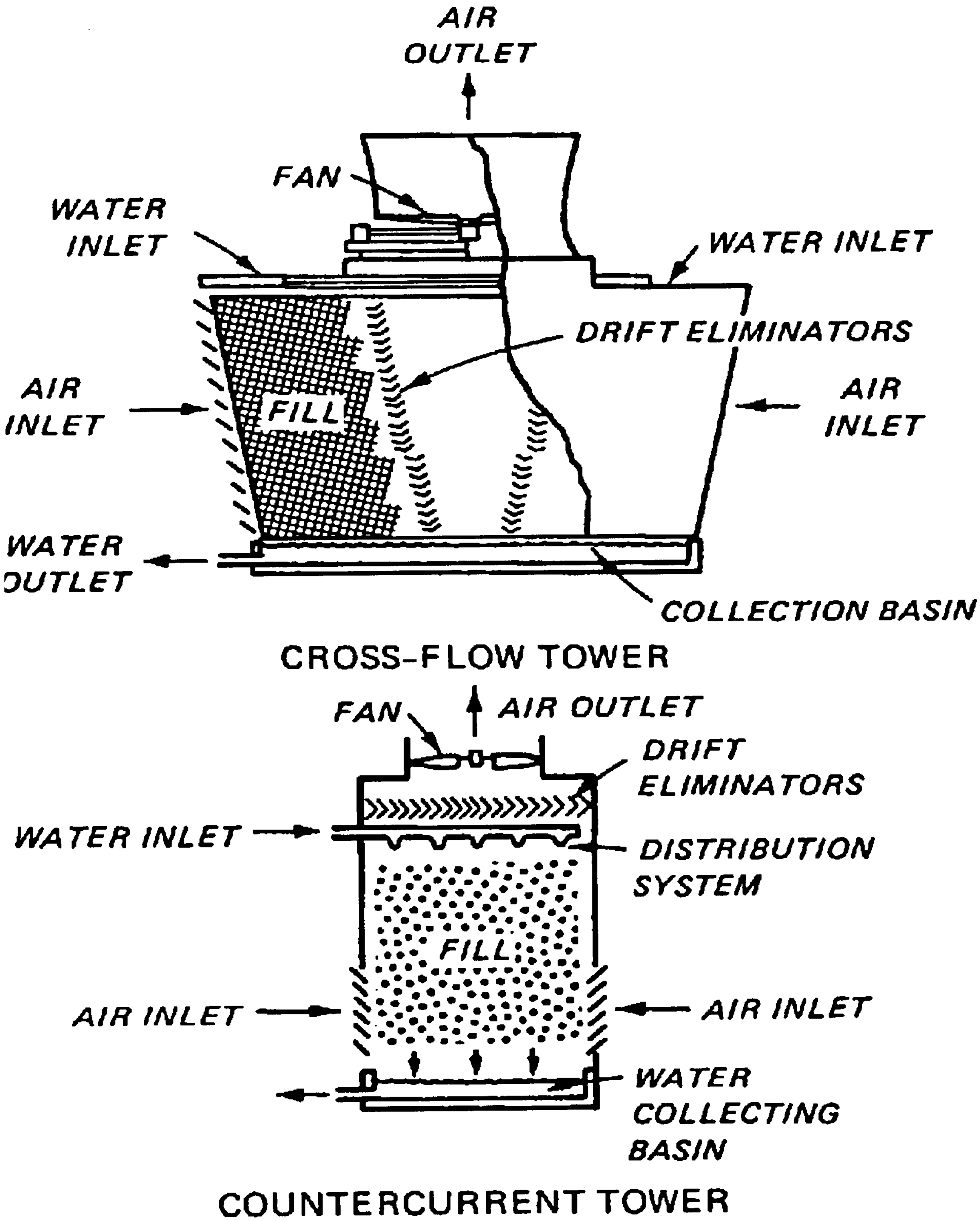


Figure 4-2. Ammonia Stripping Tower

(a) Liquid loading rate, L, lb H_2O/hr/sq ft (Kg $H^2O/hr/m^2$).

(b) Gas loading rate, G, lb air/hr/sq ft (Kg/hr/m^2).

(c) Tower width, W, or diameter, D, ft (m).

(d) Excess capacity factor.

(4) Packing characteristics (from manufacturer).

(a) Packing height of a transfer unit versus gas/liquid ratio (G/L), ft (m).

(b) Height of a transfer unit for cooling versus gas and liquid loading rates, ft (m).

(c) Pressure drop characteristics as function of gas loading.

(5) Henry*s law. Constants for chemicals to be stripped, H, atm.

d. <u>Design Criteria</u>.

(1) Air stripping can be carried out either in a stripping lagoon or in a packed column. The major factors affecting performance and design include pH, temperature, airflow, hydraulic loading, and tower packing depth and spacing. Cost and performance are relatively independent of influent ammonia concentrations. For materials like ammonia, the pH must be raised to a point where all or nearly all ammonia is converted from ammonium ion NH^+_4 to NH_3 gas. The pH for efficient operations varies from about 10.8 to 11.5. Where lime precipitation is part of a treatment scheme, it is advantageous to locate the ammonia stripping unit after lime precipitation to take advantage of the high pH in the clarifier effluent.

(2) As water temperature decreases, it becomes more difficult to remove volatiles by stripping. The amount of air per gallon (m^3) must be increased to maintain removal as temperature decreases. It is impractical to heat stripping units when the temperature reaches freezing.

(3) The hydraulic loading rate in a packed tower is a critical factor in determining performance. If hydraulic loading becomes too high, good droplet formation needed for efficient stripping is disrupted. If the rate is too low, packing may not be properly wetted, resulting in poor performance and formation of scale. To determine the packing height required in an air stripping column use equation 4-1.

$$Z_T = \frac{L}{K_{La}} * \frac{r}{(R-1} * \ln \frac{X_T/X_B * (R-1) + 1}{R} \qquad (4\text{-}1)$$

where

Z_T = packing height, m (ft)

L = liquid loading rate, kg/hr/m^2 (lb H_2O/hr/sq ft)

X_T = contaminant influent concentration, mg/ℓ

X_B = contaminant effluent concentration, mg/ℓ

K_{La} = mass transfer coefficient

$$\frac{K_{La}}{D} = \alpha \left(\frac{L}{\mu_L}\right)^{1-n} \left(\frac{\mu_L}{\rho_L^D}\right)^{0.5}$$

where

μ_L = liquid viscosity, kg/m/hr (lb/ft/hr)

D_L = density of liquid, kg/m^3 (lb/ft^3)

D = diameter of column, m (ft), determined experimentally

R = stripping factor

$$R = \frac{G * P_a/M_a}{L * P_w/M_w} * \frac{H}{P_T}$$

where

G = air loading rate, kg/hr/m^2 (lb/hr/sq ft)

P_a= air density, 1.205 g/m^3 @ 20 °C (0.075 lb/ft^3 @ 70°F)

M_a = molecular weight of air, 28.84, gmw

P_w = liquid density, 998.2 kg/m^3 @ 20 °C (62.3 lb/ft^3 @ 70 °F)

M_w = molecular weight of water, 18, gmw

H = Henry*s law constant, atm

P_T = operating pressure, atm, 1.0 at sea level

(4) Where ammonia concentrations are high (in excess of 100 mg/l), it may be attractive both economically and environmentally to recover the ammonia in an adsorption tower. With good countercurrent contact, 90 to 95 percent of

the ammonia can be transferred to the adsorption solution. Figure 4-3 illustrates the ammonia removal and recovery process.

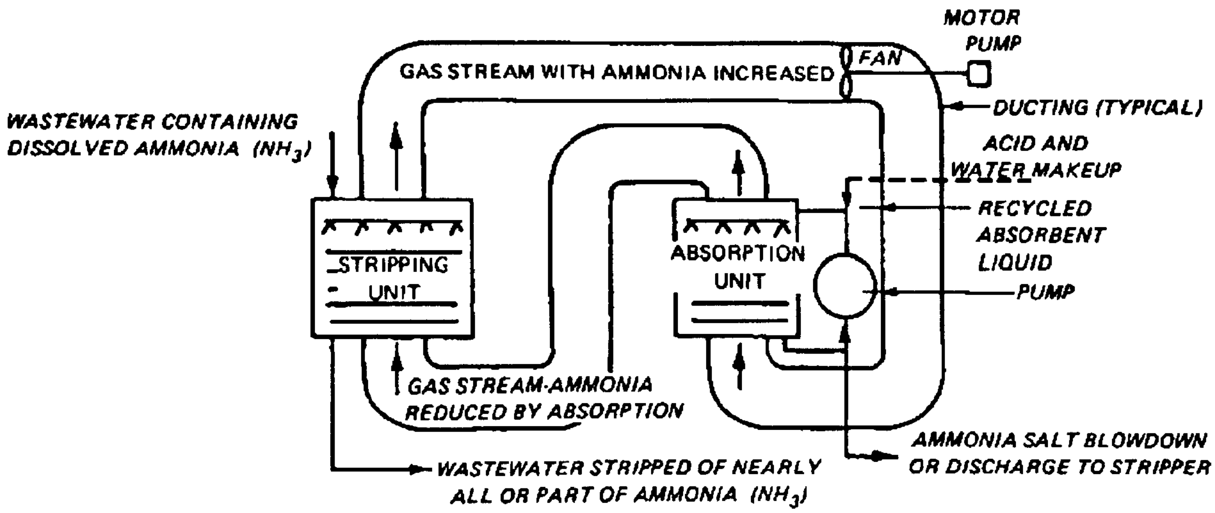


Figure 4-3. Ammonia Stripper and Recovery System

(5) When used for treatment of waters containing volatile organics, air stripping results in off gasses that may exceed regulatory criteria. Off gas treatment systems such as activated carbon or thermal destruction using incineration or catalytic oxidation may be required.

4-5. <u>Biological Treatment</u>.

a. <u>Background</u>.

(1) The major objectives of biological treatment of leachate and contaminated ground water are to reduce the dissolved organic content, to remove heavy metals and nutrients such as nitrogen and phosphorus, and to coagulate and remove colloidal solids. The major treatment effects are caused by incorporation of these materials into microorganisms* tissues. The microorganisms can either be attached to media (trickling filters, rotating biological contactors, or anaerobic filters), or settled out and discarded (lagoons and stabilization ponds), or recycled (activated sludge systems). The biological unit processes are listed in Table 4-1.

(2) Most organic chemicals are biodegradable, although the relative ease of biodegradation varies widely. With properly acclimated microbial populations, adequate detention time, and equalization to ensure uniform flow, biological treatment can be used to treat many organics. There is considerable flexibility in biological treatment because there are several available processes, and microorganisms are remarkably flexible. Several generalizations can be made about the biological treatment of organics:

Table 4-1. Summary of Biological Treatment Processes

Treatment method	Feed stream requirements and limitations	Major design and performance criteria	Environmental impact	Technology status	Reliability
Activated sludge	Can handle BODs of 10,000 mg/ℓ (10,000 ppm) Required low level of suspended solids--usually 1 percent Oil and grease should be less than 50 mg/ℓ Effective for readily degradable organics or organics to which it can be acclimated Sensitive to heavy metals	Detention time Organic load Food-to-microorganism ratio Aeration	Generates excess sludge containing refractory organics and metals that have been sorbed	Highly developed; widely used	Process reliability is very good in absence of shock loads
Pure oxygen-activated sludge	Requires suspended solid levels of about 1 percent or less Can handle higher organic loads than conventional activated sludge and is more tolerant of shock loads Sensitive to heavy metals and oil and grease	Detention time Organic load Food-to-microorganism ratio Oxygen requirements	Generates sludge containing refractory organics and sorbed metals	Relatively new technology but demonstrated for some industrial wastewaters	Reliability fully established; complex and requires high level of maintenance

(Continued)

Table 4-1. (Continued)

Treatment method	Feed stream requirements and limitations	Major design and performance criteria	Environmental impact	Technology status	Reliability
Aerobic, anaerobic, aerated, or facultative	Requires very low suspended solids (0.1 percent) Requires low strength organic wastes (except anaerobic) Sensitive to heavy metals and oil and grease	Detention time Depth Organic load Ph Oxygen levels	May create odors; may release volatiles, H_2S, and methane if anaerobic; must be lined to prevent seepage into ground water	Well demonstrated for stabilization of organics but not widely used	High if proper Ph maintained and organic load is low; sensitive to shock loads since no sludge recycled
Rotating biological contactor	Suitable for treatment of readily degradable organics; can handle higher organic loads than trickling filter but lower than activated sludge Better suited to treatment of suspended or colloidal organics rather than soluble Sensitive to oil and grease and metals	Detention time Hydraulic load Organic load Temperature Number of stages and trains	Generated sludge containing refractory organics and sorbed metals; may cause odors	Process is relatively new, not widely used but gaining in popularity	Moderate in the absence of high organic loads and temperatures below 12.8 °C (55 °F)

(Continued)

Table 4-1. (Concluded)

Treatment method	Feed stream requirements and limitations	Major design and performance criteria	Environmental impact	Technology status	Reliability
Trickling filter	Can handle only very low organic loads as compared to activated sludge	Media type Hydraulic load	Generates sludge that contains refractory organics and sorbed metals; causes odors	Widely used as a roughing filter for industrial wastes	Fair for secondary treatment; moderate as a roughing filter
	Better suited to treating suspended and colloidal organics rather than soluble ones	Organic load Bed depth Temperature			
	Sensitive to metals and oil and grease	Recirculation			

(a) nonaromatic (noncyclic) hydrocarbons are more easily treated than aromatics;

(b) materials with unsaturated bonds, such as alkenes, are more easily treated than materials with saturated bonds;

(c) stereochemistry affects the susceptibility of certain compounds to attack

(d) soluble organics are usually more readily degraded than insoluble materials; dissolved or colloidal materials are generally more readily degraded than insoluble materials. Dissolved or colloidal materials are more readily attacked by enzymes; and

(e) the presence of key functional groups at certain locations can affect the degradation rate of compounds; alcohols, for example, are more easily degraded than their alkane or alkene homologues. On the other hand, addition of a Cl group or an NO_2 group increases resistance to biodegradation.

(3) Although many compounds in leachate and contaminated ground water may be resistant at first to biological treatment, microorganisms can be acclimated to degrade many of these. Similarly, while heavy metals hinder biological treatment, the biomass can also be adjusted, within limits, to tolerate higher concentrations of metals. Concentrations of metals above which the treatment efficiency of biological processes may lessen are as follows:

Material	Inhibitory threshold (mg/ℓ)
Ammonia	480
Arsenic	0.1
Cadmium	1 to 5
Calcium	2500
Chromium (+3)	10
Chromium (+6)	1 to 10
Copper	1 to 10
Iron (+3)	15
Lead	10
Manganese	10
Mercury	0.1 to 5
Nickel	1 to 2.5
Silver	0.03
Vanadium	10
Zinc	1 to 10

b. Suspended Growth (Activated Sludge). Activated sludge is a heterogeneous suspended growth microbial culture composed largely of bacteria, protozoa, rotifers, and fungi. The bacteria are responsible primarily for assimilating most of the organic material from the waste; the protozoa and rotifers complete the process by removing the dispersed bacteria that otherwise would escape in the plant effluent, giving high COD and suspended solids. Aeration can be by air or by pure oxygen. Activated sludge systems are usually made up of several unit processes, including primary sedimentation, an aerated reactor with sludge recycle, and clarification in a settling tank. A diagram of a typical activated sludge system is presented in Figure 4-4.

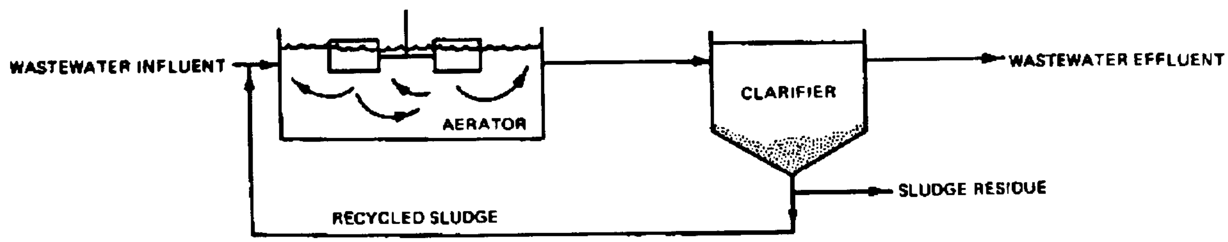


Figure 4-4. Typical Activated Sludge System (Source: Arthur D. Little, Inc. 1976).

(1) Applications.

(a) The air-activated sludge process has proven effective in the treatment of industrial wastewaters from refineries and coke plants, or pharmaceutical wastes, PVC wastes, and food processing wastes. Conventional activated sludge has treated petroleum wastes with a BOD_5 as high as 10,000 ppm.

(b) The process has also been reasonably well demonstrated for the treatment of leachate from municipal landfills. At the GROWS landfill in Bucks County, Pennsylvania, BOD removal of over 98 percent was achieved for an influent concentration of almost 5,000 milligrams per liter. Treatment included physical/chemical as well as biological treatment. Experiments have shown that activated sludge is generally well suited to treatment of high strength leachates containing high concentrations of fatty acids. As the landfill stabilizes, the ratio of BOD/COD decreases and the wastes become less amenable to biological treatment.

(c) The activated sludge process is sensitive to suspended solids and oil and grease. It is recommended that suspended solids be less than one percent. Oil and grease must be less than 75 milligrams per liter, and preferably less than 50 milligrams per liter, for effective treatment.

(2) Advantages/disadvantages. The advantages and disadvantages of both air- and pure-oxygen-activated sludge treatment are summarized below:

Advantages	Disadvantages
Activated sludge has been widely used in industrial waste water treatment	Capital costs are high
Numerous process variations which allow for high degree of flexibility	Process is sensitive to suspended solids, fats and oils, and metals
Process reliability is good (although not well known for pure-oxygen-activated sludge)	Generates sludge which can be high in metals and refractory organics
Can tolerate higher organic loads than most biological treatment processes	Subject to upsets from shock loads
	Fairly energy intensive
	O&M intensive

(3) Data requirements. Principal data requirements for the design of a activated sludge system include:

(a) Specific BOD reaction rate coefficient (for retention time).

(b) Oxygen coefficients (for oxygen requirements).

(c) Sludge coefficients (biodegradable fraction).

(d) Biodegradable sludge fraction.

(e) Oxygen transfer coefficient.

(f) Standard oxygen transfer efficiency.

(g) Oxygen saturation coefficient.

(h) Temperature correction coefficient.

(i) Average and maximum influent flow.

(j) Influent temperature.

(k) Extreme ambient temperature, summer and winter.

(l) Average and maximum influent BOD.

(m) Influent suspended solids.

(4) Design criteria.

(a) Key design parameters for activated sludge include aeration period of detention time; BOD loading per unit volume, usually expressed in terms of pounds BOD applied per day per g BOD/m^2 (1,000 cubic feet) of aeration basin;

and the food-to-microorganism ratio (F/M), which expresses BOD loading with regards to microbial mass (MLVSS). There are several modifications of the activated sludge process that may be used depending upon the BOD loading and the required treatment efficiency. Table 4-2 summarizes the loading and operational parameters for aeration processes that may be applicable to treatment of hazardous leachate.

(b) Even though conventional treatment has limitations such as poor tolerance for shock loads, a tendency toward producing bulking sludge that results in high suspended solids in the effluent, and low acceptable BOD loadings, these problems can be alleviated to varying extents with variations in process design. The completely mixed activated sludge (CMAS) modification of the process (Table 4-2) is the most widely used for treatment of waste-waters with relatively high organic loads. The advantages of this system are:

! Less variation in organic loading, resulting in more uniform oxygen demand and effluent quality.

! Dilution of the incoming wastewater into the entire basin, resulting in reduced shock loads.

! Uses the entire contactor contents at all times because of complete mixing.

(c) The extended aeration process involves long detention times and a low F/M ratio (0.1). Process design at this low F/H ratio results in a high degree of oxidation and a minimum of excess sludge. The contact stabilization process--in which biological solids are contacted with the wastewater for short periods of time, separated, and finally aerated to degrade absorbed organics--has shown some success for industrial wastes with a high content of suspended and colloidal organics. Pure oxygen systems have resolved several major drawbacks of conventional treatment. Pure oxygen systems show increased bacterial activity, decreased sludge volume, reduced aeration tank volume, and improved sludge settling. The pure oxygen process has been demonstrated to be applicable to a wide range of wastes at high F/M ratios. Such wastes streams include: petrochemical, dye, pharmaceutical, and pesticide wastes.

(d) In addition to process variations, there are several measures available for minimizing process upsets and maximizing stability:

! The deleterious effects of hydraulic and organic load variations can be minimized by equalization preceding biological treatment.

! A commonly used method for providing increased biodegradation is to increase the inventory of biological solids in the aeration basin by increasing the sludge-recycle ratio or reducing sludge wastage. However there is usually a tradeoff to such an approach. Higher sludge quantities lead to increased need for food and air. Also, old heavy sludge tends to become mineralized and devoid of oxygen, creating a less active floc. The rate of return sludge may vary from 35 to 50 percent in systems carrying a low MLSS concentration (approximately 2,000 milligrams per liter) and from 75 to 100 percent in systems carrying higher MLSS.

Table 4-2. Summary of Operating Parameters for Air-Activated Sludge and Pure-Oxygen-Activated Sludge

Process mobilization	Aeration system	BOD loading g BOD/m^3 (lb BOD/ 1,000 ft^3)	FM ratio g BOD/day g MLVSS (lb BOD/day lb MLVSS)	Mixed liquor suspended solids (mg/ℓ)	Applications and limitations
Conventional	Diffused air, mechanical aerators	320-640 (20-40)	0.2-0.4 (no conversion required)	1,500-3,000	Low strength wastes; subject to shock load
Step aeration	Diffused air	640-960 (40-60)	0.2-0.4	2,000-3,500	Flexible and generally applicable to a wider range of wastes than conventional treatment. Uses lower volumes of air and shorter detention times than conventional processes, but can handle higher BOD loads
Complex-mix	Diffused air, mechanical aerators	800-1920 (50-120)	0.2-0.6	3,000-6,000	Resistant to shock loads, generally applicable
Extended aeration	Diffused air, mechanical aerators	160-400 (10-25)	0.05-2.0	3,000-6,000	Requires long detention times and low organic load; produces low volume of sludge; available as package plant
Contact stabilization	Diffused air, mechanical	960-1200 (60-75)	0.2-0.6	1,000-3,000[1] 4,000-10,000[2]	Low aeration requirements; not suitable for soluble BOD

(Continued)

[1] Contact unit.
[2] Solids stabilization unit.
(Source: Hammer 1975, Metcalf and Eddy, Inc. 1972, Nemerow 1978).

Table 4-2. (Concluded)

Process mobilization	Aeration system	BOD loading g BOD/m^3 (lb BOD/ 1,000 ft^3)	FM ratio g BOD/day g MLVSS (lb BOD/day lb MLVSS)	Mixed liquor suspended solids (mg/ℓ)	Applications and limitations
High rate	Mechanical aerators	1280+ (80+)	0.5-1.0 (no conversion required)	4,000-10,000	Well suited to shock loads; requires little supervision. However, requires long detention times, requiring three times as much air as conventional treatment
Pure-oxygen	Mechanical aerators	1920+ (120+)	0.6-1.5	6,000-8,000	High efficiency possible at increased BOD loads and reduced aeration

! Suspended solids should be reduced as much as possible by sedimentation or filtration.

! Since kinetics of biological degradation are concentration-dependent, dilution can minimize process upsets under some conditions.

! Sludge bulking, which leads to poor effluent quality, can be controlled by pH adjustment, sufficient aeration, and adequate nutrient supply. An important consideration for leachate treatment is that microbial growth is a function of the limiting nutrient. Some leachates may be phosphorus or nitrogen limited. Requirements for nitrogen and phosphorus are generally

N = 5 kg/100 kg BOD_5 (5 lb/100 lb BOD_5) removed

P = 1 kg/100 kg BOD_5 (1 lb/100 BOD_5) removed

(e) Equipment used for activated sludge treatment varies considerably, but the major types of aerators are mechanical surface, diffuse air, and sparged turbine aerators.

! Mechanical surface aerators are most economical but have the lowest transfer rates.

! Compressed air diffusers: Coarse air diffusers have lower energy requirement and lower gas transfer efficiency. Fine air diffusers have higher energy requirement and higher gas transfer efficiencies.

! Sparged turbine aerators use most energy but have best gas transfer efficiency. This form of diffused air is very fine and benefits from improved gas transfer kinetics.

(f) Secondary clarifiers are used to separate activated sludge solids from the mixed liquor and to produce concentrated solids for the return flow required to sustain biological treatment. Average hydraulic loading varies from 1.6 to 3.3 $m^3/day/m^2$ (400 to 800 gallons per day per square foot) and peak loadings range from 2.9 to 4.9 $m^3/day/m^2$ (700 to 1,200 gallons per day per square foot), depending on MLSS concentration and percent sludge recycle. Average solids loading of 2.9 to 5.9 $kg/hr/m^2$ (0.6 to 1.2 pounds per hour per square foot) and peak loadings of 6.1 to 9.8 $kg/hr/m^2$ (1.25 to 2.0 pounds per hour per square foot) are typical for activated sludge plants. Depths are normally 3.7 to 4.6 m (12 to 15 feet).

c. <u>Fixed Film (Trickling Filter)</u>. Trickling filters are a form of biological treatment in which a liquid waste of less than 10,000 mg/ℓ suspended solids is trickled over a bed of rocks or synthetic media upon which a slime of microbial organisms is grown. The microbes decompose organic matter aerobically; these conditions are maintained at the outer slime surface by updrafts of air. Some anaerobic decomposition may occur at the interior surface adjacent to the trickling bed media. Periodically, the slime layer sloughs off due to the weight of the microbial growth or the hydraulic flow rate of the effluent. A schematic diagram of a typical trickling filter treatment system appears in Figure 4-5.

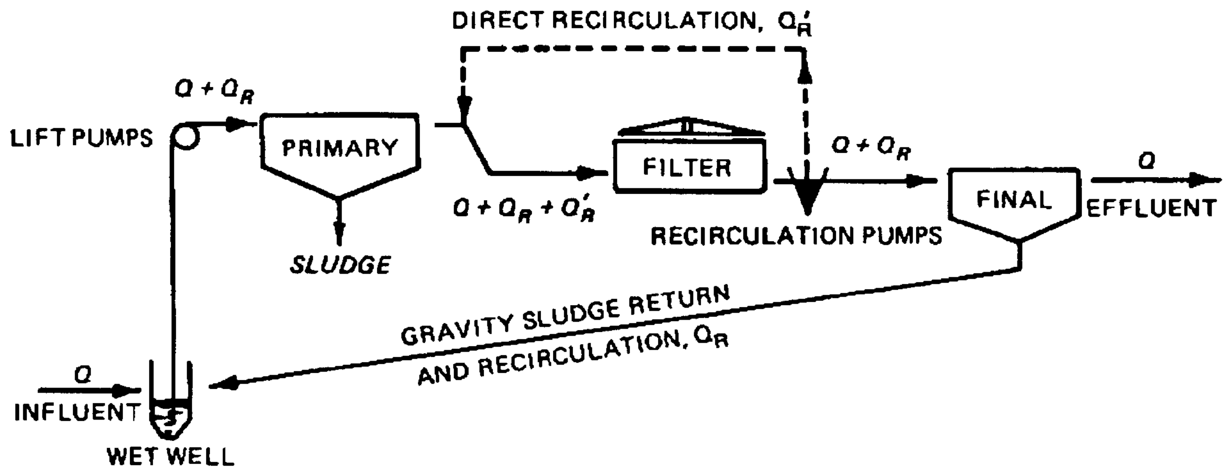


Figure 4-5. Trickling Filter Recirculation (Source: Hammer 1975, EPA 1982)

(1) Applications.

(a) Trickling filters are well suited to treatment of low flow waste streams and are often used as roughing filters to reduce organic loads to a level suitable for activated sludge treatment. Trickling filters are currently used in conjunction with other treatment methods to treat wastewaters from refineries, pharmaceuticals, pulp and paper mills, etc. Efficiency of trickling filters in the treatment of refinery and petrochemical wastes ranges from 10 to 20 percent when used as a roughing filter to 50 to 90 percent when used for secondary treatment. The process is more effective for removal of colloidal and suspended materials than it is for removal of soluble matter.

(b) Because of the short hydraulic residence time on the filter material, biodegradation along the filter media is generally insufficient as the sole means of biological treatment. For concentratrated wastes, a high rate of recirculation would be required for significant reduction of organics. The short residence time, however, has the advantage of allowing greater variations in influent waste composition as compared with activated sludge or anaerobic digestion. By placing a trickling filter in sequence with activated sludge treatment, the filters could be used to equalize loading variations while the activated sludge would achieve the high removal efficiencies needed.

(2) Advantages/disadvantages. Advantages and disadvantages of trickling filters as compared to other biological treatment methods and nonbiological methods for removal of organics are as follows:

Advantages	Disadvantages
Because of short hydraulic residence times, process is not highly sensitive to shock loads	Vulnerable to below-freezing temperatures
Suitable for removal of suspended or colloidal matter	Limited treatment capability in a single-stage operation
Has good applicability as a roughing filter to equalize organic loads	Potential for odor problem
	Has limited flexibility and control
	Requires long recovery time if disrupted
	Requires large surface area compared with other biological treatment systems

(3) Data requirements. The data required for trickling filter design are generally the same as for activated sludge with the exception of no requirements for biodegradable sludge fraction, average MLVSS, and nonbiodegradable fraction. Summer and winter ambient conditions are required, these include:

(a) Temperature.

(b) Wind velocity.

(c) Insolation-solar radiation.

(d) Relative humidity.

(4) Design citeria.

(a) The variables that influence design and performance of the trickling filter include: organic and hydraulic load, media type, nature of the waste, pH, and temperature. Trickling filters are classified according to their ability to handle hydraulic and organic loads. Typical design criteria for low and high rate filters are shown in Table 4-3. Use of plastic media filters with low bulk density has resulted in increased organic and hydraulic loading rates over those achieved with rock media filters. Plastic media filters have generally shown good performance under high BOD loading conditions that would not be tolerated by a conventional-type system because of clogging problems.

Table 4-3. Design Criteria for Trickling Filters

Design Parameter	Plastic media filter	High rate, rock media	Low rate, rock media
Hydraulic loading, $m^3/day/m^2$ ($gal/day/ft^2$)	2.9-5.7 (700-1,400) (secondary) 9.4-18.9 (2,3000-4,600) (roughing filter)	.94-3.7 (230-900)	0.1-.37 (25-90)
Organic loading lb BOD/day/ 1,000 ft	10-50 (secondary) 100-500 (roughing filter)	20-60	5-20
Bed depth, ft	20-30	3-6	5-10
Media type	Plastic	1- to 5-in. rock	1- to 5-in. rock

(Source: EPA 1982).

(b) Recirculation is generally required to provide uniform hydraulic loading as well as to dilute high-strength waste waters. However, there is a limit to the advantage achievable with recirculation. Generally, recirculation rates greater than four times the influent rate do not increase treatment efficiency. Several recirculation patterns are available. One of the most popular is gravity return of the underflow from the final clarifier to a wet well during periods of low flow and direct recirculation by pumping filter discharge back to the influent as shown in Figure 4-5.

(c) Several formulas have been proposed which predict BOD removal efficiency based on waste type, influent BOD, hydraulic load, and other factors related to performance. Problems with these models include the need to determine treatability on a case-by-case basis and the fact that the models are usually applicable for only very specific conditions.

(d) The National Research Council (NRC) formulation to predict BOD removal efficiency was the result of an extensive analysis of operational records from stone-media trickling filter plants at military installations. The NRC data analysis is based on the fact that the amount of contact between the filter media and organic matter depends on the filter dimensions and the number of passes, and that the greater the effective contact, the greater will be the efficiency. However, the greater the applied load, the lower will be the efficiency. Therefore, the quantity that primarily determines efficiency in a trickling filter is a combination of effective contact and applied load. The efficiency through the first or single stage (E_1) and through the second stage (E_2) can be predicted from equations 4-2 and 4-3.

$$E_1 = \frac{100}{1 + 0.0085\left(\frac{W_1}{VF}\right)^{\frac{1}{2}}} \qquad (4\text{-}2)$$

$$E_2 = \frac{100}{1 + \frac{0.0085}{1-E_1}\left(\frac{W_2}{VF}\right)^{\frac{1}{2}}} \qquad (4\text{-}3)$$

where

E_1 = percent ROD removal efficiency through the first-stage filter and settling tank

W_1 = BOD loading (lb/day; 1 lb/day = 0.45 Kg/day) to the first- or second-stage filter, not including recycle

V = volume (acre-ft; 1 acre ft = 1,233.5 m^3) of the particular filter stage (surface area times depth of media)

F = number of passes of the organic material, equal to

(1 + R/I)/[l + (1 - P)R/I]

where R/I equals the recirculation ratio (recirculated flow/plant influent flow), and P is a weighting factor which, for military trickling filter plants, was found to be approximately 0.9

E_2 = percent BOD removal efficiency through the second-stage filter and settling tank

W_2 = BOD loading (lb/day) to the second-stage filter, not including recycle

(Note: Empirical equations, can only be used with English units - to use with metric, must convert to English before putting in Equation.)

(e) If recirculation is not being used, F will equal 1. It should be remembered that the NRC formulation was based on military waste water which is characteristically more concentrated than average domestic waste water. This could make the NRC formula more applicable to hazardous waste treatment. The effect of temperature on performance was not considered since most of the plants studied were in the middle latitudes of the United States.

d. Rotating Biological Disks. A rotating biological disk (RBD) is a fixed film biological method for treating effluent containing organic waste, similar in operating principle to trickling filters. A series of disks (1.8 to 3.0 in (6 to 10 feet) in diameter), or drums in some configurations, coated with a microbial film, rotate at 0.5-15 revolutions per minute through troughs containing the effluent; 40-50 percent of the disk surface area is immersed in the effluent while the uncovered portion of the disk exposes the microbial film to the atmosphere during each rotation. Supplemental aeration is sometimes beneficial. The shearing motion of the disk through the effluent keeps the biological floc from becoming too dense. Periodic reversing of drum rotation is often used to control biological growth. The disks are usually arranged in series in groups of four. A schematic of a RBD is shown in Figure 4-6.

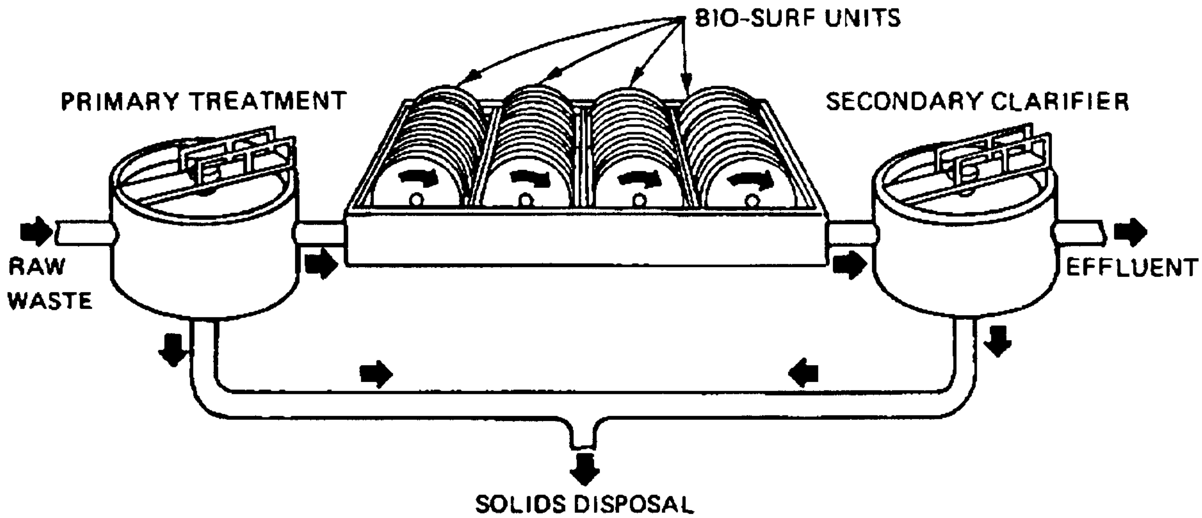


Figure 4-6. Rotating Biological Disk Treatment Schematic

(1) Applications. Rotating biological disks are currently being used at full scale to treat waste waters from the manufacture of herbicides, pharmaceuticals, petroleum, pulp and paper, and pigments and may have application for ground-water or leachate treatment at hazardous waste sites. They also have found use for domestic waste-water treatment. The process has only been used in the United States since 1969. Its modular construction, low hydraulic head loss, and adaptability to existing plants have resulted in growing use. The process can be used for roughing, nitrification, or secondary treatment.

(2) Advantages and disadvantages. Avantages and disadvantages of rotating biological disks as compared to trickling filters and activated sludge are summarized below:

Advantages	Disadvantages
Process has considerably more flexibility than trickling filters; both the intensity of contact between biomass and waste water and the aeration rate can be easily controlled by the rotational speed of the disks	Vulnerable to climate changes if not covered
	High organic loads may result in first-stage septicity and supple mental aeration may be required

(Continued)

Advantages	Disadvantages
Waste-water retention time can be controlled by selecting appropriate tank size; thus higher degrees of treatment can be obtained than with trickling filters	Odor may be a problem if septic conditions develop
In contrast to the trickling filter, biological disks rarely clog since shearing forces continuously and uniformly strip excess growth	As with trickling filters, biomass will be slow to recover if disrupted
As compared with activated sludge, rotating biological disks can handle large flow variations and high organic shock loads	Can handle only relatively low-strength wastes as compared with activated sludge
Modular construction provides flexibility to meet increased or decreased treatment needs	
Low O&M and energy requirements	
Requires small surface area when compared with other biological systems	

(3) Data requirements. The data required for the design of rotating biological disks are generally the same as for trickling filter design.

(4) Design criteria. For adequate treatment it is recommended that the process include four stages (disks) per train and the use of at least two parallel trains. Based on the design criteria, rotating biological disks can handle organic loads similar to a high-rate trickling filter. Typical design criteria include:

	(Without nitrification)	(With nitrification)
Organic Loading:	480-960 g BOD/m^3 (30-60 lb BOD/1,000 ft^3 media)	240-320 g BOD/m^3 (15-20 lb BOD/1,000 ft^3 media
Hydraulic Loading:	3×10^{-3} to 6.1×10^{-3} m^3/day/m^2 (0.75 to 1.5 gal/day/ft^2)	1.2×10^{-3} - 2.5×10^{3} m^3/day/m^2 (0.3-0.6 gal/day/ft^2)
Detention Time:	40-90 min	90-230 min

e. Lagoon Treatment. Lagoons or waste stabilization ponds are systems in which the processes of microbial oxidation, photosynthesis, and sometimes anaerobic digestion combine to break down hazardous organic compounds. They are similar to activated sludge units without sludge recycling. Aeration may be supplied passively by wind and algae or, in aerated lagoons, by mechanical aerators or diffused air. The ecology of lagoons closely resembles a natural eutrophic lake, a more complex system than other biological treatment systems. A secondary benefit of lagoons is clarification. Physical and chemical treatment processes may also be carried out in lagoons. Figure 4-7 shows a flow diagram of an aerated lagoon, with a secondary clarifier. A separate clarifier may not be required with other lagoon designs, e.g., facultative lagoons, if the design includes a separate baffled settling compartment, two or more lagoons in series, or other special features.

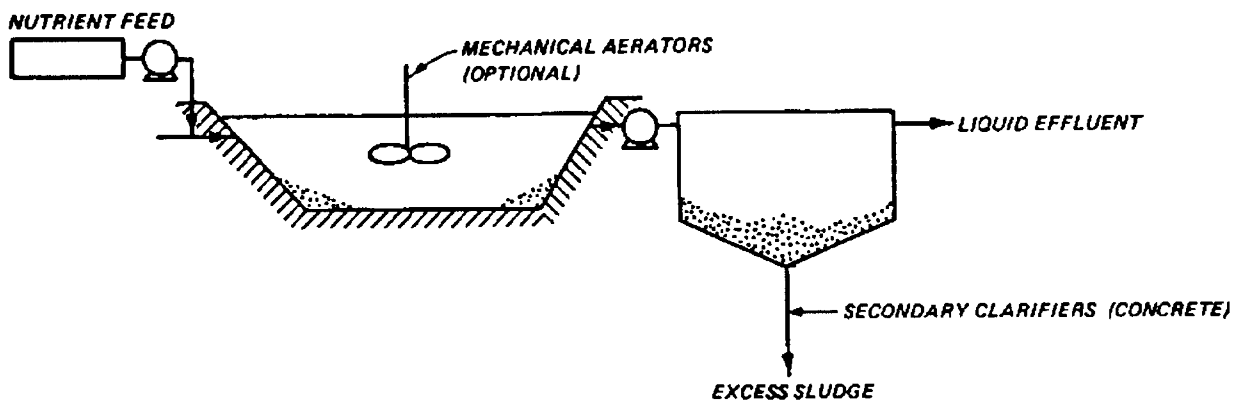


Figure 4-7. Aerated Lagoon (Polymeric-Lined Earth Construction)

(1) Applications. Waste stabilization ponds have been used to treat low-strength industrial wastes, landfill leachate, and as a polishing step for certain waste types. This treatment module is employed in food processing industries, paper and pulp mills, textile mills, refineries, and petrochemical plants.

(2) Advantages/disadvantages. The advantages and disadvantages of stabilization ponds and aerated lagoons are as follows:

Advantages	Disadvantages
Operating costs are low compared with other biological treatment methods	Tolerate low-strength wastes only
	Intolerant of suspended solids and metals
Cost-effective treatment for polishing effluent	Require large land areas
Waste stabilization ponds require minimal energy	Performance markedly affected by temperature, and treatment method is not suitable for freezing temperatures

(Continued)

Advantages	Disadvantages
	System has limited flexibility
	Volatile gases may be emitted from processes

(3) Data requirements. The data requirements are generally the same as those for activated sludge systems. The nonbiodegradable fraction and average MLVSS are not required; however, the summer and winter ambient conditions will affect performance.

(4) Design criteria.

(a) Each subtype of waste stabilization pond utilizes a different type of bacteria but is of similar construction, with an earthen pit and earthen side levees. Treatment of leachates requires that the pond be lined. The designs of various waste stabilization ponds and anaerobic lagoons differ significantly. Table 4-4 summarizes the major design criteria. The criteria indicate that, in general, lagoons can treat only low-strength waste and therefore will be best suited as a polishing step used in conjunction with other treatment methods.

(b) As Table 4-4 indicates, the aerobic lagoon requires the greatest surface area to treat an equivalent waste load. Oxygen transfer depends on the ratio of lagoon surface area to volume (length-to-width ratio should be less than 3:1), temperature, turbulence, and bacterial oxygen uptake. The system has the least tolerance for high organic loads but benefits from a short detention time. Anaerobic stabilization ponds require significantly less surface area and can handle substantially higher organic loads. Deep lagoons benefit from better heat retention, and an effluent length-to-width ratio of 2:1 is recommended.

(c) Sludge buildup is much less for the anaerobic pond than that for the aerobic; for every Kg (pound) of BOD destroyed by the anaerobic process, about 0.1 Kg (pound) of solids is formed, as compared to 0.5 Kg (pound) for the aerobic lagoon. The major disadvantage of the anaerobic lagoon is that it produces strong odors unless the sulfate concentration is maintained below 100 milligrams per liter.

(d) The facultative lagoon benefits from having an aerobic layer that oxidizes hydrogen sulfide gas to eliminate odors. It can handle BOD loads intermittently between the anaerobic and aerobic lagoon.

(e) Artificial aeration with mechanical or diffused aerators allows for deeper basins and higher organic loads than those obtained in aerobic lagoons. The basins are designed for partial mixing only, and anaerobic decomposition occurs on the bottom. Operating costs are significantly less than those for activated sludge, but the system cannot withstand the organic loads tolerated by activated sludge. In general, the use of several lagoons in series is more

Table 4-4. Design Criteria for Waste Stabilization Ponds[1]

Design parameter	Aerobic	Facultative	Anaerobic	Aerated
Depth, m (ft)	0.27 to 0.55 (0.9 to 1.8)	0.55 to 1.4 (1.8 to 4.5)	2.3 to 5.5 (7.5 to 18)	9.1 to 5.5 (3 to 18)
Organic load, kg/ha/day (lb BOD/acre/day)	100 to 200 (89.3 to 178.6)	10-to 100 (8.93 to 89.3)	200 to 2000 (178.6 to 1786)	10 to 31 (8.93 to 267.9)
Detention time typical, days	2 to 6	7 to 30	30 to 50	3 to 10
Influent BOD, mg/ℓ	200	200 to 500	500 and up	200 to 500
Flow regime	Intermittently mixed	Mixed surface layer	Not mixed	Completely mixed
Principal conversion product	Algae, CO_2, bacteria	Algae, CO_2, CH_4, bacteria	CO_2, CH_4, bacteria	CO_2, bacteria
Algal concentration, mg/ℓ	40 to 100	10 to 80	0 to 5	--
Operating pH	6.5 to 10.5	6.5 to 9.0	6.8 to 7.2	6.5 to 8.0
Effluent suspended solids, mg/ℓ	10 to 140	40 to 100	80 to 160	80 to 250

[1] Adapted from EPA (1979), Liptak (1974), and Metcalf and Eddy, Inc. (1979).

efficient than one lagoon since it can reduce short-circuiting and lead to increased organic removal efficiency.

4-6. Carbon Adsorption.

a. Process Description.

(1) Activated carbon, granular or powdered, when contacted with water containing organic material, will remove these compounds selectively by a combination of adsorption of the less polar molecules, filtration of the larger particles, and partial deposition of colloidal material on the exterior surface of the activated carbon. Adsorption results from the forces of attraction between the surface of a particle and the soluble organic materials that contact the particle. As a result of the activation process, activated carbon has a large surface area per unit weight, making it a very efficient adsorptive material. It has long been used to remove taste and odor-causing impurities from public water supplies. More recently, activated carbon adsorption has been used in waste-water treatment as a tertiary process following conventional secondary treatment or as one of several unit processes comprising physical-chemical treatment. Pesticides and other long-chain organics have excellent adsorption characteristics on activated carbon.

(2) The most efficient and practical use of activated carbon in waste-water treatment has been in fixed beds of granular activated carbon. A typical adsorption system consists of several adsorption trains operated in parallel. Each train contains two adsorbers arranged for series flow. The waste water is applied to the adsorbers at a flow rate ranging from 1.6×10^{-2} to 3.3×10^{-2} $m^3/min/m^2$ (4 to 8 gallons per minute per square foot). Contact time (empty bed residence time) ranges from 15 to 35 minutes depending on the desired effluent quality. Countercurrent flow systems allow systems to approach activated carbon isotherm capacity and are recommended.

(3) To minimize suspended solids collection which can clog the pores and reduce adsorber capacity, the carbon adsorption system should be preceded by media filtration. Provisions must be made to regularly backwash the adsorption system to flush out accumulated suspended solids and biological growth. A good design practice is to allow for a bed expansion of up to 50 percent. Flow rates during backwash should range from 6.2×10^{-2} to 8.2×10^{-2} $m^3/min/m^2$ (15 to 20 gallons per minute per square foot). Biological growth can be controlled effectively by chlorination of the influent to the adsorber or by chlorination during the backwash operation.

(4) When the active sites on the carbon particles have been filled, the effluent quality deteriorates and the carbon must be regenerated or replaced. It is not economical to have onsite regeneration for systems requiring regeneration of less than about 91 kg (200 pounds) of carbon per day. For larger systems, a regeneration system should be provided. A typical regeneration system includes: (a) hydraulic transport of the carbon to the regeneration unit, (b) dewatering of spent carbon, (c) heating of carbon to oxidize or volatilize the adsorbed impurities, (d) water cooling of the carbon, (e) water washing and hydraulic transport back to the adsorbers, and (f) scrubbing of

furnace off-gasses. The most common type of furnace in use is the multiple hearth furnace.

(5) Input such as the minimum contact time, optimum flow rate, head loss at various flows, backwash rate, and required carbon dosage should be obtained from onsite pilot plant carbon column tests. Where this is not possible, accepted design criteria should be used to generate the required input data. Static isotherm tests conducted in the laboratory are not sufficient.

b. Applications.

(1) The suitability of carbon adsorption for treatment of waste water associated with disposal sites depends upon the influent characteristics, the extent of pretreatment, and the required effluent quality. The highest concentration of solute in the influent stream that has been treated on a continuous basis is 10,000 mg/ℓ (10,000 ppm TOC), and a 1 percent solution is currently considered as the upper limit.

(2) Concentrations of oil and grease in the influent should be limited to 10 mg/ℓ (10 ppm). Concentrations of suspended solids should be less than 50 mg/ℓ (50 ppm) in upflow systems; downflow systems can handle concentrations as high as 2,000 mg/ℓ (2,000 ppm), although frequent backwashing would be required. Removal of inorganics by carbon generally requires concentrations of less than 1,000 mg/ℓ (1,000 ppm) and preferably less than 500 mg/ℓ (500 ppm).

(3) The suitability of using activated carbon for removal of a specific solute depends upon its molecular weight, structure, and solubility. Table 4-5 summarizes the influence of molecular structure and other properties of organics on their adsorbability. Table 4-6 summarizes the potential for removal of inorganics by activated carbon.

(4) As would be expected from the information in Table 4-5, activated carbon has been proven effective in the removal of a variety of chlorinated hydrocarbons, organic phosphorus, carbonates, PCBs, phenols, and benzenes. Specific hazardous organics that are effectively removed include aldrin, dieldrin, endrin, DDD, DDE, DDT, toxaphene, and two aroclors. A granular activated carbon system was used as part of the treatment system for the Bridgeport, New Jersey, remedial action. Mobile carbon systems have also been used successfully for several years.

(5) Activated carbon treatment has not been shown to be suitable for treatment of municipal landfill leachates from young landfills; carbon shows poor adsorption capacity for fatty acids, which are prevalent in municipal landfill leachate. Carbon adsorption is generally not effective for wastes with high BOD/COD and COD/TOC ratios.

c. Advantages/disadvantages. The advantages and disadvantages of carbon absorption are summarized below:

Table 4-5. Effects of Molecular Structures and Other Factors on Adsorption by Activated Carbon

1. Aromatic compounds are generally more adsorbable than aliphatic compounds of similar molecular size.

2. Branched chains are usually more adsorbable than straight chains.

3. Substituent groups affect adsorbability:

Substituent group	Nature of influence
Hydroxyl	Generally reduces adsorbability; extent of decrease depends on structure of host molecule
Amino	Effect similar to that of hydroxyl but somewhat greater. Many amino acids are not adsorbed to any appreciable extent
Carbonyl	Effect varies according to host molecule; glyoxylic and more adsorbable than acetic but similar increase does not occur when introduced into higher fatty acids
Double bonds	Variable effect
Halogens	Variable effect
Sulfonic	Usually decreases adsorbability
Nitro	Often increases adsorbability

4. An increasing solubility of the solute in the liquid carrier decreases its adsorbability.

5. Generally, strongly ionized solutes are not as adsorbable as weakly ionized ones; i.e., undissociated molecules are, in general, preferentially adsorbed.

6. The amount of hydrolytic adsorption depends on the ability of the hydrolysis to form an adsorbable acid or base.

7. Unless the screening action of the carbon pores intervenes, large molecules are more sorbable than small molecules of similar chemical nature. This is attributed to more solute carbon chemical bonds being formed, making desorption more difficult.

Table 4-6. Potential for Removal of Inorganic Material by Activated Carbon

Constituents	Potential for removal by carbon
Metals of high sorption potential	
Antimony	Highly sorbable in some solutions
Arsenic	Good in higher oxidation states
Bismuth	Very good
Chromium	Good, easily reduced
Tin	Proven very high
Metals of good sorption potential	
Silver	Reduced on carbon surface
Mercury	CH_3HgCl sorbs easily, metals filter out
Cobalt	Trace quantities readily sorbed, possibly as complex ions
Zirconium	Good at low pH
Elements of fair-to-good sorption potential	
Lead	Good
Nickel	Fair
Titanium	Good
Vanadium	Variable
Iron	Fe^{3+} good, Fe^{2+} poor, but may oxidize
Elements of low or unknown sorption potential	
Copper	Slight, possibly good if complexed
Cadmium	Slight
Zinc	Slight
Beryllium	Unknown
Barium	Very low
Selenium	Slight
Molybdenum	Slight at pH 6-8, good as complex ion
Manganese	Not likely, except as MnO
Tungsten	Slight
Miscellaneous inorganic water constituents	
Phosphorus	
P, free element	Not likely to exist in reduced form in water
PO_4^{3-} phosphate	Not sorbed but carbon may induce precipitation $Ca_3(PO_4)_2$

(Continued)

Table 4-6. (Continued)

Constituents	Potential for removal by carbon
Free halogens	
F_2 fluorine	Will not exist in water
Cl_2 chlorine	Sorbed well and reduced
Br_2 bromine	Sorbed strongly and reduced
I_2 iodine	Sorbed very strongly, stable
Halides	
F^- Fluoride	May sorb under special conditions
Cl^-, Br^-, I^-	Not appreciably sorbed

Advantages	Disadvantages
High flexibility in operation and design	Intolerant of high suspended solids levels
Suitable for treatment of a wide range of organics that do not respond to biological treatment	Carbon can be "poisoned" by high heavy metals concentrations which will affect organic adsorption
Has high adsorption potential for some highly hazardous inorganics (e.g., Cr, Cn)	Requires pretreatment for oil and grease removal where concentrations are greater than 10 mg/ℓ (10 ppm)
Tolerant of some fluctuations in concentrations and flow	Not suitable for removal of low molecular weight organics, highly soluble or highly ionized organics
	Limited to wastes with less than 10,000 mg/ℓ (10,000 ppm) organics
	O&M costs are high

d. Data requirements. Data requirements are as follows:

(1) The waste stream average daily flow.

(2) The waste stream contaminant concentrations.

(3) Carbon physical properties (bulk density) and the amount lost during one regeneration cycle (if regeneration is included in design).

(4) Hydraulic loading rate (usually 8.2×10^{-3} to 3.3×10^{-2} $m^3/min/m^2$ (2 to 8 gallons per minute per square foot)).

(5) Organic removal rate, adsorption efficiency, and adsorption rate constant.

(6) The backwash hydraulic loading (if backwashing is included in design).

e. Design criteria.

(1) Critical design criteria are organic load, hydraulic load, contacting method, contact time, and regeneration requirements. The approximate carbon requirements for a specific organic load, and the residual organic levels can be roughly estimated from adsorption removal kinetics conducted on a batch basis. An isotherm can be used as a functional expression for variation of adsorption with concentration of adsorbate in bulk solution. The Freundlich isotherm is expressed in terms of removal of impurity (i.e., BOD, COD, or color).

$$\frac{X}{M} = KC^{1/n} \qquad (4\text{-}4)$$

where

X = impurity adsorbed

M = weight of carbon

C = equilibrium concentration of impurity

K,n = constant (Culp et al. 1978)

(2) Isotherms are a useful approximation of treatability, but generally give a falsely high estimate of continuous carbon performance. A continuous-flow pilot carbon treatment system is generally a prerequisite of design except on an emergency basis.

(3) There are four basic ways that waste streams can be contacted, and the choice of the appropriate method depends upon influent characteristics, effluent criteria, flow rate, and economics. Table 4-7 summarizes these available methods, and Figure 4-8 illustrates them. Figure 4-9 illustrates a process flow diagram with upflow carbon contactors and regeneration. Typical operating parameters for carbon adsorption systems are summarized in Table 4-8. The parameters are based on system operations for physical/chemical and tertiary treatment systems.

(4) The decision to regenerate and reuse granular carbon or to use it on a once-through basis is made primarily on economics. Toxicity of the absorbed chemicals can also affect this decision; however, for plants requiring less than 91 kg (200 pounds) per day of carbon (less than approximately 3032 m^3/day (0.8 million gallons per day)), regeneration is probably not

Table 4-7. Summary of Activated Carbon Contacting Methods

Method	Comments
Downflow adsorbers in parallel	For high volume applications Can handle higher than average suspended solids (65-70 mg/ℓ (~65-70 ppm)) Relatively low capital costs Effluents from several columns blended, therefore less suitable where effluent limitations are low 8.2×10^{-3}-4.1×10^{-2} $m^3/min/m^2$ (2-10 gpm/ft^2) flow rate
Downflow adsorbers in series	Large volume systems Countercurrent carbon use Effluent concentrations relatively low Can handle higher than average suspended solids (65-70 mg/ℓ (~65-70 ppm)) if downflow Capital costs higher than for parallel systems 8.2×10^{-3}-4.1×10^{-2} $m^3/min/m^2$ (2-10 gpm/ft^2)
Moving bed	Countercurrent carbon use (most efficient use of carbon) Suspended solids must be low (10 mg/ℓ (<10 ppm)) Capital and operating costs relatively high Can use such beds in parallel or series 4.1×10^{-3}-2.9×10^{-2} $m^3/min/m^2$ (1-7 gpm/ft^2) flow rate
Upflow-expanded series	Countercurrent carbon use (if in series) Can handle high suspended solids (they are allowed to pass through) High flows in bed (6.2×10^{-2} $m^3/min/in^2$ —15 gpm/ft^2)) Minimum pretreatment Minimum headloss

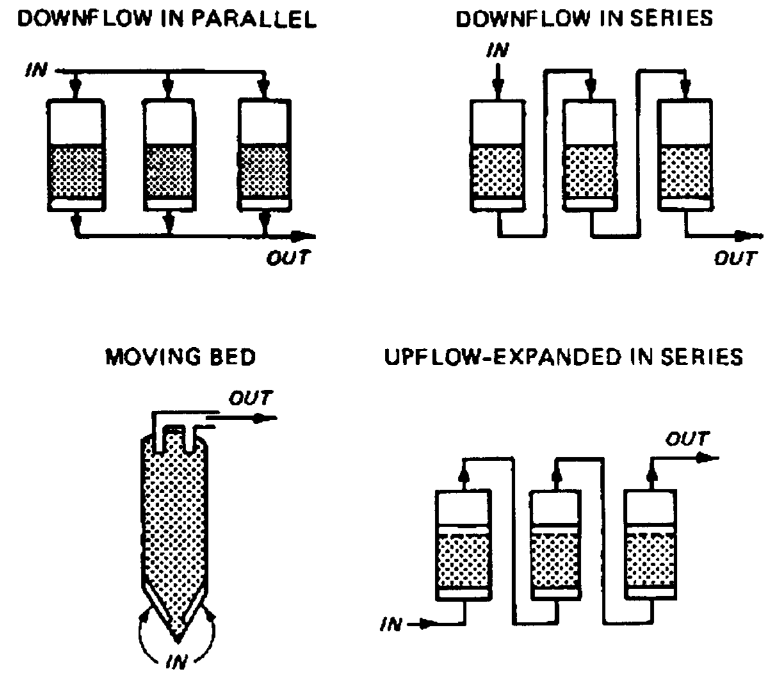


Figure 4-8. Most Common Configuration of Activated Carbon Adsorber Systems

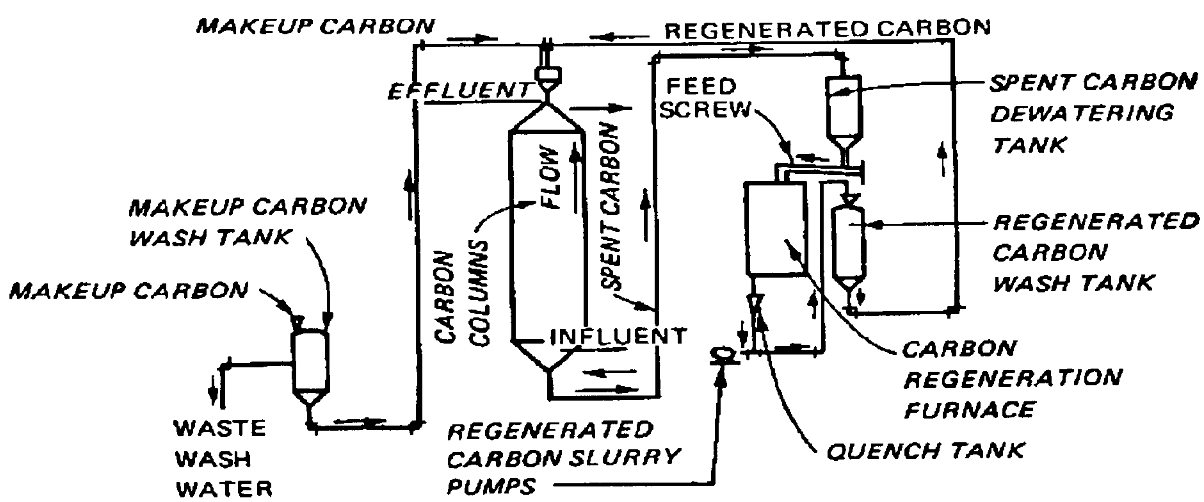


Figure 4-9. Process Flow Diagram with Upflow Carbon Contactors and Regeneration

Table 4-8. Operating Parameters for Carbon Adsorption

Parameter	Requirements
Contact time	Generally 10-50 min; may be as high as 2 hr for some industrial wastes
Hydraulic load	8.2×10^{-3}-6.2×10^{-2} $m^3/min/m^2$ (2-15 gpm/ft^2) depending on type of contact system, see Table 4-7
Backwash rate	Rates of 8.2×10^{-3}-4.1×10^{-2} $m^3/min/m^2$ 920-30 gpm/ft^2) usually produce 25-50 percent bed expansion
Carbon loss during regeneration	4-9 percent 2-10 percent
Weight of COD removed per weight of carbon	0.2-0.8
Carbon requirements	
PCT plant	60-216 mg/ℓ (500-1,800 $lb/10^6$ gal)
Tertiary plant	24-60 mg/ℓ (200-500 $lb/10^6$ gal)
Bed depth	3-9.1 m (10-30 ft)

economical. Most leachate and ground-water treatment facilities will fall within this range. Use of electric furnaces, rather than multiple-hearth furnaces, may make it possible to regenerate activated carbon economically for plants using less than 200 pounds per day. Regeneration needs can be determined on the basis of COD adsorbed per pound of carbon or required carbon dosage in terms of total flow.

4-7. Chemical Oxidation.

a. Process Description.

(1) Oxidation reactions are among the most important chemical reactions with which the engineer deals. They are involved in a wide range of laboratory analyses as well as water and waste-water treatment. No oxidation reaction occurs without a concomitant reduction reaction and vice versa.

(2) Chemical oxidation is a process in which the oxidation state of a substance is increased. Conversely, chemical reduction is a process in which the oxidation state is reduced.

(3) Even though redox reactions are applicable to metals and nonmetals, organics and inorganics, the discussion here will be directed largely to

organics and nonmetals. Applications of oxidation are at present largely limited to potable water treatment, specialized industrial water and waste-water treatment, and high-level tertiary waste treatment.

(4) Due to the costs involved, oxidation reactions are usually carried out only for pretreatment or post-treatment. For pretreatment, the objective is usually to remove specific compounds or groups, cleave organic molecule chains, and/or detoxify such as to make the waste suitable for biological treatment. Post-treatment operations are usually carried out to remove residual BOD to meet stringent effluent requirements.

(5) Oxidizers most often used in waste-water treatment include the following:

(a) Oxygen or air (21 percent oxygen).

(b) Ozone.

(c) Chlorine and hypochlorites.

(d) Chlorine dioxide.

(e) Hydrogen peroxide.

(f) Potassium permanganate.

(6) Oxygen-molecular oxygen is a weak oxidizing agent when compared to others mentioned. It is mentioned here primarily due to its attractive cost. The use of molecular oxygen may be limited to the oxidations of certain metals such as iron and manganese. However, it is sometimes reported to remove BOD by chemical oxidation. These reductions are probably the result of a stripping action as opposed to actual oxidation. Air sparging would be expected to remove volatile gases such as carbon dioxide, hydrogen sulfide, methane, and certain other low-boiling organic compounds.

(7) Ozone is a powerful oxidizing agent, as illustrated by the following redox potentials:

$$O_3 + 2H^+ + 2e^- \rightarrow O_2 + H_2O \qquad E_o = 2.07v$$

$$1/2\ Cl_2 + e^- \rightarrow Cl^- \qquad E_o = 1.36v$$

It is sufficiently strong to break many carbon-carbon bonds and even to cleave aromatic ring systems, e.g., conversion of phenol to three molecules of oxalic acid. Complete oxidation of some organic species to CO_2 and H_2O can be expected if ozone dosage is sufficiently high. However, some materials show almost complete resistance to ozone attack. A Refractory Index (RFI) has been defined so as to provide pertinent information on the relative reactivity of ozone with a variety of materials. The RFI is defined as the pounds of ozone per pound of contaminant that would be required to bring about 50 percent conversion of oxidation in one hour. RFI values for a cross-section of compounds are shown in Table 4-9. Several compounds are resistant to ozone,

Table 4-9. Resistance of Selected Species to Ozone Oxidation

Compound	O_3[1]	UV/O_3[2]
KCN	0.41	-
Color (units)	0.66	-
Complexed Cd- cyanide	0.96	-
Phenol	4.4	-
Ammonium ion	8	-
Glycine	19.7	6.0
Ammonium palmitate	27.3	7.2
Glycerol	112	7.4
Ethanol	245	41.0
Complexed ferricyanide	270	8.6
Acetic acid	1,000	47.0

[1]Pounds of ozone per pound of contaminant required for 50 percent conversion.
[2]Pounds of ozone per pound of contaminant with addition of ultraviolet light required for 50 percent conversion.

acetic acid for example. Carboxylic acids, in general, are resistant to chemical oxidation. Typical treatment efficiencies are listed in Table 4-10.

(a) Typically, oxidation reactions will not be carried out to completion due to physical restraints on the ozone-contaminant system and due to economics involved. Since only partial oxidations will occur, it is important to know the types of end products remaining. Some expamles are given in Table 4-11.

(b) Ozone is not stable in either the gaseous form or in solution. Decomposition in the gas phase generally increases with temperature and is catalyzed by solid alkalies, metals, metal oxides, carbon, and moisture.

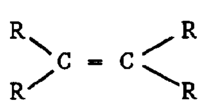
(c) Many redox reactions are pH dependent. However, ozone is an exception and is relatively insensitive to pH. One exception is that of converting cyanide to carbon dioxide. This reaction requires a pH of about 9 before ozonation.

(d) Ultraviolet light has been shown to provide a powerful synergistic action with ozone. The result of this phenomenon is also shown in Table 4-9. Compounds that showed essentially no reactivity with ozone showed at least partial degradation with the addition of ultraviolet light. Ultraviolet light can also generate ozone from oxygen in the air.

Table 4-10. COD Reduction by Ozone

Compound	Concentration (g/ℓ)	Volume treated (liters)	O_3 (g/hr)	%COD reduction for given hours of treatment time						
				2	3	6	8	12	16	24
Acetic acid	1	3	2.45	0	0	0	0	0	0	0
Benzyl alcohol	1	1	0.5	10	26	--	58	--	--	--
Diethylene glycol	1	3	1.47	18	27	27	30	30	30	30
Ethylene diamine	1	1	0.5	7	26	--	33	--	--	--
Ethylene glycol	1	1	0.5	9	17	--	31	--	--	35
Formalin	5.0	3	2.28	10	20	29	36	44	48	53
Glycine	1.0	3	1.0	10	0	0	0	0	0	0
Hydroquinone	1	1	0.5	25	46	--	--	--	--	--
Hydroxylamine sulfate	1	3	1.88	41	58	67	72	77	78	--
Maleic acid	(not given)	3	2.44	62	73	79	83	89	92	95
Menthol	1	3	2.12	8	13	17	21	27	31	37
Potassium ferricyanide	11.0	2	4.0	1	2	3	4	6	7	11
Sodium formate	2.0	3	1.4	42	63	75	83	93	98	--
Sodium thiocyanate	1	1	0.5	88	90	90	--	--	--	--
Sodium thiosulfate	1	1	0.5	94	97	--	--	--	--	--

Table 4-11. Products of Ozonation of Various Compounds

Species	Ozonation product	Comments
Chromium (III) Cr^{+3}	Chromium (VI) CrO_3	
Cyanide CN^- (free)	Cyanate CNO^-	Cyanate can be further degraded to CO_2
Ferrocyanide $Fe(CN)_6^{-4}$	Ferricyanide $Fe(CN)_6^{-3}$	Used in regeneration of photo bleach
Ammonia NH_3	Nitrate NO_3^-	Fairly slow
Dimethyl sulfide CH_3SCH_3	Dimethyl sulfoxide $CH_3\overset{O}{S}CH_3$	Reduces or eliminates odor problems
Amine $(CH_3CH_2CH_2CH_2)_3N$	Amine oxide $(CH_3CH_2CH_2CH_2)_3NO$	
Alcohol CH_3OH	Aldehyde CH_2O	
Aldehyde CH_2O	Carboxylic acid $HCOOH$	Evidence for stepwise oxidation is clear
Carboxylic acid CH_3COOH	No reaction	
Phenol C_6H_5 OH	Oxalic acid $\begin{matrix}COOH\\ \vert \\COOH\end{matrix}$	By way of quinone and intermediate, unsaturated acids
Alkene 	Aldehydes, ketones, carboxylic acids $R_2C = O$ $RCOOH$ $RHC = O$	

(8) Hydrogen peroxide.

(a) Hydrogen peroxide is a moderate strength chemical oxidant compared to chlorine. It does not produce chlorinated oxidation products species, however, and may be preferable to chlorine in many instances. Its lower oxidizing potential can result in selective reactions to oxidize a specific pollutant (e.g., H_2S) without oxidizing a wide spectrum of other organic and inorganic compounds also present in the mixture. Consumption of hydrogen peroxide can be significantly less than many other common oxidants. In dilute solution (<30 percent), the decomposition of hydrogen peroxide is accelerated by the presence of metal ion contaminants. Industrial strength hydrogen peroxide (>30 percent) can catalyze these contaminants in violent decomposition.

(b) Hydrogen peroxide can oxidize many chemicals present in contaminated ground water and leachates. Examples of these chemicals are: hydrogen sulfide and mercaptans, phenol in liquid or gas, ferrous iron, photo waste-silver, thiosulfate, cyanide, and hypochlorite (chlorine residual). Mercaptans and sulfides are usually the cause of odor complaints, may be toxic, and can result in corrosion of metals and concrete. Hydrogen peroxide can detoxify specific compounds by organic ring cleavage, stripping substituent groups, or oxidizing specific items such as sulfur. Treatment may also improve the biodegradability of wastes.

(c) A summary of the primary oxidants used in waste-water treatment and their identified applications is presented in Table 4-12.

b. Advantages/Disadvantages. Advantages and disadvantages of chemical oxidation are shown below:

Advantages	Disadvantages
Effective on dilute waste streams	Higher treatment costs than comparable biological treatment systems
Can be used to detoxify and improve biodegradability and adsorption characteristics	Some organics are resistant to most oxidants
	Inorganics such as chloride will interfere with the oxidation reaction
	Partial oxidation may generate toxic compounds

c. Data Requirements. Data requirements for the chemical oxidation process will depend upon the objective of the treatment and the oxidation potential and reactivity of the waste. In general, the necessary data can only be determined by bench or pilot scale testing. Typical data needs are listed below:

Table 4-12. Waste Treatment Applications for Selected Oxidants

Oxidant	Waste
Oxygen or air	Sulfites ($SO_3^=$)
	Sulfides ($S^=$)
	Ferrous iron (Fe^{++})
	very slow
	Manganese (Mn^{++})
	Carbon dioxide (CO_2)
	Methane (CH_4)
Ozone	Cyanides (CN^-)
	Color
	OH
	Phenol
	Ammonia (NH_3)
	fairly slow
	Chromium (Cr^{+3})
	Amines
	Alcohols
	Aldehydes
	Alkenes
Chlorine and hypochlorites	Sulfides ($S^=$)
	Mercaptans
	Cyanide (CN^-)
	Lead (Pb)
	Nitrite (NO_2^-)
	Manganese (Mn^{++})
	Ferrous iron (Fe^{++})
Chloride dioxide	Cyanide (CN^-)
	Diquat pesticides
	Paraquat
	Sulfide ($S^=$)
	Aldehydes
	Amines (tertiary)
	Mercaptans
	Phenol
Hydrogen peroxide	Phenol
	Cyanide
	Sulfides
	Sulfites
	Lead
	Ferrous iron
	Sulfates
	Hypochlorite
	Mercaptans

(1) Effectiveness of various oxidants for the specific waste to be oxidized.

(2) Reaction time required and dosage of oxidant necessary to produce adequate destruction.

(3) Optimum pH.

(4) Interfering species in the waste.

(5) Pretreatment requirements.

(6) Resulting product toxicity.

(7) Requirement for catalysts.

(8) Light absorption characteristics in ultraviolet (UV) area.

d. Design Criteria.

(1) The UV-ozone chemical oxidation system shows promise for hazardous waste treatment due to its high reaction potential. UV-ozone will oxidize most organics, cleave carbon-carbon bonds, oxidize substituent groups, and open aromatic rings.

(2) There are several critical characteristics associated with the use of UV light. Short-wavelength UV light is required to provide sufficient energy to properly excite the molecule to be oxidized. Almost any medium through which the light passes will attenuate the light energy. The lamp and sleeves must be constructed from a special quartz to transmit the short wavelengths. The depth of the fluid being treated should be minimized. In order for the molecule to be excited and oxidized, it must be capable of absorbing light in the UV band.

(3) The surface of the quartz sleeves in contact with process fluid tends to become fouled. Some manufacturers provide a traveling rake to continuously clean these surfaces.

(4) A reaction time of 30 minutes to 1 hour is usually sufficient for most designs but this must be confirmed through pilot plant testing. Agitation increases effectiveness and should be provided where feasible.

(5) The dose of ozone or other chemical oxidant can be estimated by theoretical calculations sufficient for planning-level calculations. A 10 to 20 percent excess is recommended. Calculations must address all of the oxidizable materials in the waste.

4-8. Resin Adsorption.

a. Process Description.

(1) Resin adsorption is a process for the removal of organic chemicals from liquid waste streams. It is somewhat similar to adsorption on activated carbon. Perhaps the most significant difference between the two is that resins are always chemically regenerated through the use of caustic, steam, or organic solvents while carbon must be thermally regenerated because of the strong adsorptive forces. Synthetic resins generally have a lower adsorption capacity, a higher initial cost, and a longer operating life.

(2) Resin adsorption should be given serious consideration:

(a) For the treatment of colored wastes; ROD and COD may be high.

(b) When material recovery is practical.

(c) Where selective adsorption is desired.

(d) Where low leakage rates are required.

(e) Where carbon regeneration is not practical.

(f) Where there are high levels of dissolved inorganic solids.

(3) Process flow sheets vary depending on the nature of the solute and the regenerant used. Organic solvents such as acetone, methanol, and isopropanol have been used for regeneration purposes. The solvent overcomes the adsorbent resin*s attractive forces which allows the adsorbed organic to diffuse into the solvent phase. A system used for the recovery of phenol using acetone as a regenerant is shown in Figure 4-10.

(4) Inorganic solvent systems used for regeneration purposes include steam, aqueous caustic solutions for removing adsorbed weak acids, and aqueous acids for removing adsorbed weak bases. A system used for the recovery of chlorinated hydrocarbon using steam as a regenerant is shown in Figure 4-11.

(5) Resin lifetimes may vary considerably depending on the nature of the feed and regenerant streams. Regeneration with caustic is estimated to cause a loss of 0.1 to 1 percent of the resin per cycle; replacement of resins at such installations may be necessary every 2 to 5 years. Regeneration with hot water, steam, or organic solvent should not affect the resins, and, in this case, lifetimes will be limited by slow fouling or oxidation resulting in a loss of capacity; actual experience indicates that lifetimes of more than 5 years are obtainable.

(6) Synthetic resins are available commercially from three manufacturers. A summary of the properties of some available resins is shown in Table 4-13. One of the more important physical properties is that of pore size. This factor may allow selective adsorption based upon molecular size.

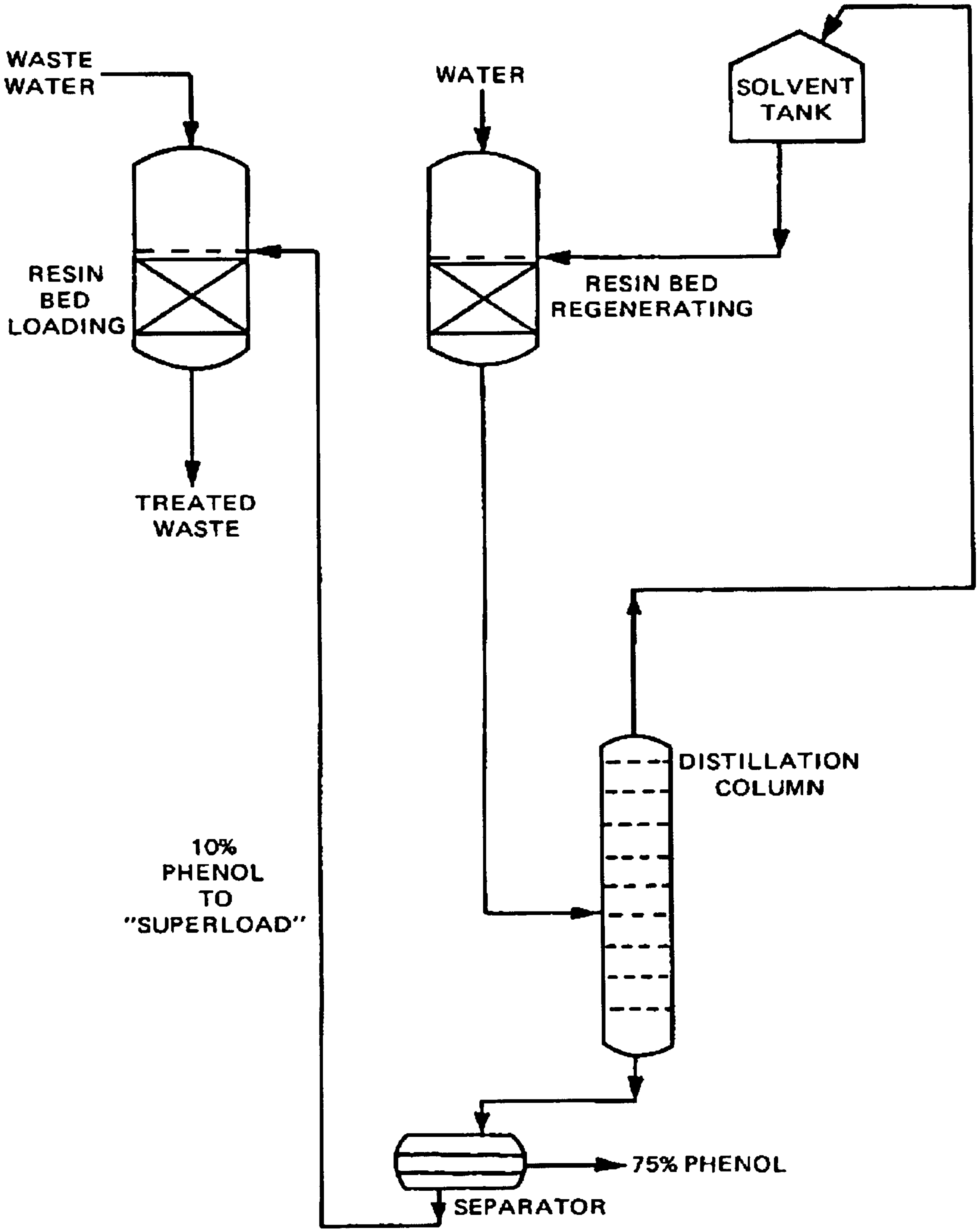


Figure 4-10. Phenol Recovery System Using Acetone Regenerant

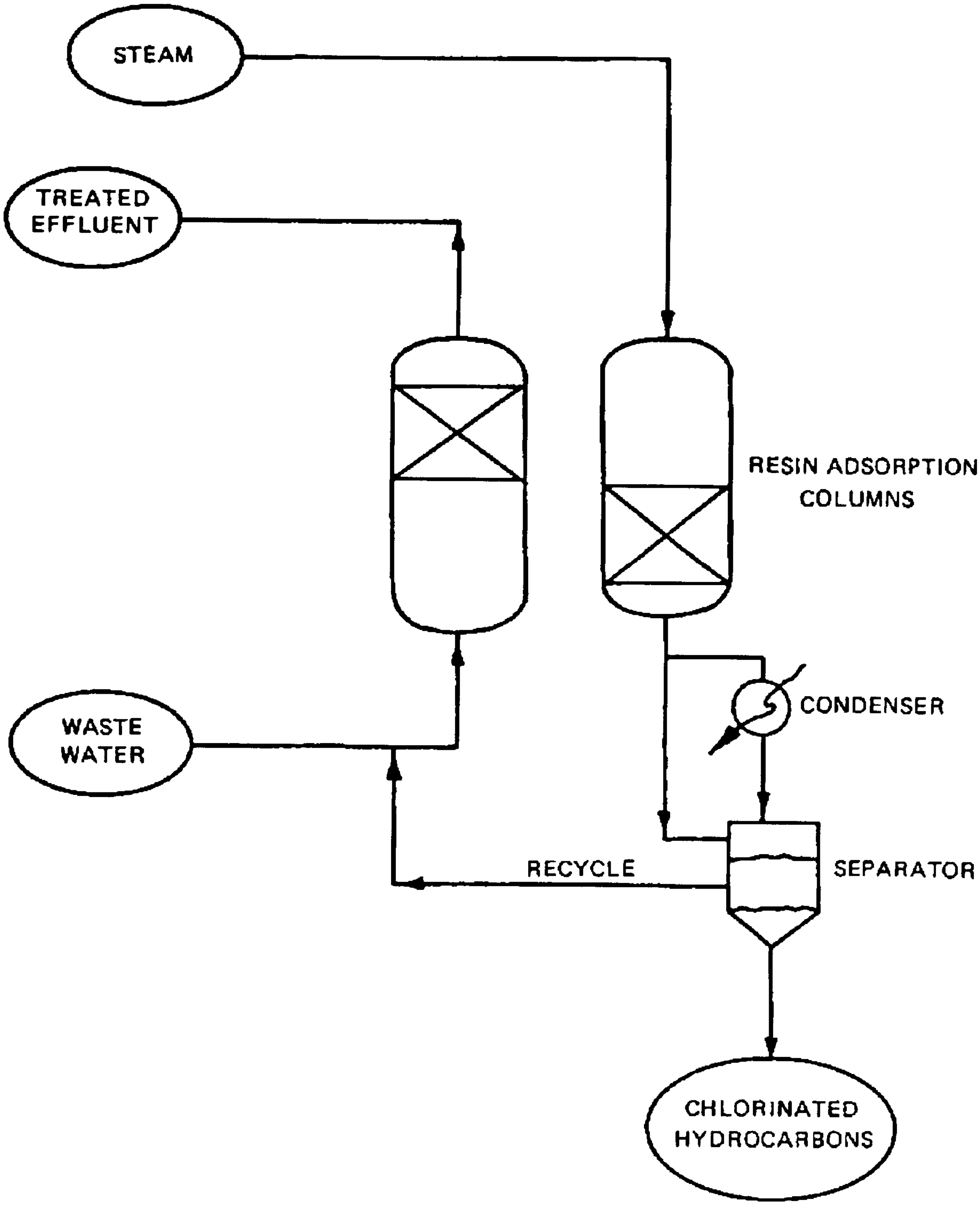


Figure 4-11. Chlorinated Hydrocarbon Recovery System Using Steam Regenerant

Table 4-13. Properties of Some Commercially Available Resin Absorbents

Resin Name[1]	Base	Specific gravity (wet)	Void volume %	Particle size mm	Bulk density kg/m^3 (pcf)	Surface area m^2/g	Average pore size A°
XAD-1		1.02	37	20-50	--	100	200
XAD-2	Styrene-divinylbenzene	1.02	42	20-50	640-704 (40-44)	300	90
XAD-4		1.02	51	20-50	624 (39)	780	50
XAD-7		1.05	55	20-50	656 (41)	450	90
XAD-8	Acrylic ester	1.09	52	20-50	688 (43)	140	235
DOW XFS 4256[2]	Styrene-divinylbenzene	--	40	10+	432 (27)	400	110
DOW XFS 4022		--	35	20-50	--	100	200
DOW XFS 4257	--	--	40	20-50	--	400	100
Duolite S-30		1.11	35	16-50	480 (30)	128	--
Duolite S-37		1.12	35-40	16-50	640 (40)	--	--
Duolite ES-561	Phenol-formaldehyde[3]	1.12	35-40	18-50	640-720 (40-45)	--	--
Duolite A-7D		--	--	--	--	--	
Duolite A-7		1.12	35-40	16-50	640 (40)	--	--

[1] XAD resins manufactured by Rohm and Haas Company; DOW XFS manufactured by Dow Chemical USA; Duolite resins manufactured by Diamond Shamrock Chemical Company.
[2] This resin is designed for use in vapor phase adsorption applications.
[3] Functional groups, such as phenolic hydroxyl groups and secondary and tertiary amines, are present on the basic phenol-formaldehyde structure. Physical form of these resins is granular as opposed to a bead for the other brands.

b. Applications.

(1) Polymeric adsorbent resins can be selected for specific applications. The surface area and pore structure can be controlled over a wide range of values. These factors are most important when the selective removal of a particular contaminant, perhaps hazardous, is desired. Also, when coupled with the weak attractive forces between solute molecules and resin product recovery may become a practical consideration. Even though overall capacities of synthetic resins may be less, capacity for a specific pollutant may be greater. This has been demonstrated for a number of pesticides.

(2) Polymeric adsorbents have been used to remove and recover a variety of toxic organic chemicals. These are as follows:

- Chlorinated pesticides.
- Phenols.
- Aliphatic chlorinated hydrocarbons.
- Aromatics (benzene, toluene, and xylene).

(3) Other reported uses include removal in dyestuff, removal of fat from meat packing operations, recovery of antibiotics, and removal of organics from brine.

c. Advantages/Disadvantages. Advantages and disadvantages of resin absorption are summarized below:

Advantages	Disadvantages
Resin can be designed for selective adsorption	Resin costs are higher than carbon
Leakage rates are much lower than for carbon	Resin cannot tolerate strong oxidizing agents
Regeneration is accomplished in situ with solvents	Usually have smaller system capacity than carbon
Resin can tolerate high levels of inorganic solvents	Pretreatment such as filtering is often necessary
Resin can operate over a wide pH range	Volume of sulvent needed for backwash may be significant

d. Data Requirements

(1) Data requirements for resin adsorption will be much the same as those for carbon adsorption. Data concerning the resin itself are available from the manufacturers.

(2) As with carbon, isotherms must be available for the particular waste or contaminant under consideration. From isotherm data, capacity of the resin can be calculated. These data provide an estimate of the level of treatability that can be expected.

(3) Due to the fact that resin adsorption is relatively new and does not presently enjoy wide applications, pilot scale column studies are also recommended. These studies are used to confirm batch studies and provide information on optimum column height, flow rates, loadings, and potential operational problems.

(4) Unlike carbon adsorption, data must be generated to determine the regeneration of the resin and the ultimate disposal of solute removed. Regeneration can be accomplished using a variety of materials including caustic, hot water, steam, and organic solvents. If organic solvents are used, a distillation step is typically included.

e. Design Criteria. As a result of limited applications, design criteria for resin adsorption are not well defined. However, some suggestions are given below:

(1) Column should be operated in the downflow mode.

(2) Suspended solids in the influent should be maintained less than 10 milligrams per liter. (A sand filter may be required to pretreat the influent.)

(3) pH may be varied between 2 and 11 depending upon adsorption characteristics.

(4) Operating temperature may be as high as 80°C but will reduce capacity of resin.

(5) High total disolved solids (TDS) in the influent do not detract from normal operations.

(6) Influent concentration of organics (C_0) should be limited as follows:

$$C_0 < (0.1)\ \frac{\text{capacity of resin}}{3 \text{ x bed volume}}$$

(7) Strong oxidants will attack the resin and must be removed.

(8) A minimum of two columns in parallel should be used; i.e., one on line and one regenerating.

(9) Flow rates through the bed should be 3.3×10^{-2} to 0.27 $m^3/min/m^3$ (0.25 to 2 gallons per minute per cubic foot) of resin or 2 to 16 bed volumes per hour.

(10) Contact times are on the order of 3 to 30 minutes.

4-9. Chemical Reduction.

a. Process Description.

(1) Chemical reduction is of interest because heavy metals in solution can often be reduced to their elemental form for potential recycling or can be converted to less toxic oxidation states. One such metal is chromium (Cr), which, when present as chromium (VI), is a very toxic material. In the reduced state, chromium (III), the hazards are lessened and in this form can be precipitated for removal. At present, chemical reduction is applied primarily to the control of hexavalent chromium in the plating and tanning industries and to the removal of mercury from caustic/chlorine electrolysis cell effluents.

(2) Reduction-oxidation, or redox, reactions are those in which the oxidation state of at least one reactant is raised while that of another is lowered. In the reaction

$$2H_2CrO_4 + 3SO_2 \rightarrow Cr_2(SO_4)_3 + 2H_2O$$

the oxidation state of Cr changes from 6^+ to 3^+ (Cr is reduced); the oxidation state of sulfur (S) increases from 2^+ to 3^+ (S is oxidized). This change of oxidation state implies that an electron was transferred from S to Cr(VI). The decrease in the positive valence (or increase in the negative valence) with reduction takes place simultaneously with oxidation in chemically equivalent ratios. Reduction is used to treat wastes in such a way that the reducing agent lowers the oxidation state of a substance in order to reduce its toxicity, reduce its solubility, or transform it into a form that can be more easily handled.

(3) The base metals are good reducing agents. Iron, aluminum, zinc, and sodium compounds are often used for the reduction treatments. In addition, sulfur compounds are also some of the more common reducing agents.

(4) Table 4-14 lists the more common reduction reactions for chromium (VI) treatment and their reaction products.

(5) The first step of the chemical reduction process is usually the adjustment of the pH of the solution to be treated. With sulfur dioxide treatment of chromium (VI), for instance, the reaction requires a pH in the range of 2 to 3. The pH adjustment is done with the appropriate acid (sulfuric, for example). This is followed by the addition of the reducing agent. Mixing is provided to improve contact between the reducing agent and the waste. The agent can be in the form of a gas (sulfur dioxide) or as a solution (sodium borohydride) or perhaps as a finely divided powder if there is adequate mixing. Reaction times vary for different wastes, reducing agents, temperatures, pH, and concentration. For commercial-scale operations

Table 4-14. Conventional Chrome Reduction Reactions

(1) <u>Cr^{+6} to Cr^{+3} using sulfur dioxide</u>

$$4SO_2 + 4H_2O \rightarrow H_2SO_3 + 2CrO_3 + 3H_2SO_3 \rightarrow Cr_2(SO_4)_3 + 3H_2O$$

$4SO_2$	$4H_2O$	H_2SO_3	$2CrO_3$	$3H_2SO_3$	$Cr_2(SO_4)_3$
sulfur dioxide	water	sulfurous acid	chromic acid	sulfurous acid	chromic sulfate

(2) <u>Cr^{+6} to Cr^{+3} using bisulfites</u>

$$4CrO_3 + 6NaHSO_3 + 3H_2SO_4 \rightarrow 2Cr_2(SO_4)_3 + 3Na_2SO_4 + 6H_2O$$

$4CrO_3$	$6NaHSO_3$	$3H_2SO_4$	$2Cr_2(SO_4)_3$	$3Na_2SO_4$
chromic acid	sodium bisulfite	sulfuric acid	chromic sulfate	sodium sulfate

(3) <u>Cr^{+6} to Cr^{+3} using ferrous sulfate</u>

$$2CrO_3 + 6FeSO_4 + 6H_2SO_4 \rightarrow 3Fe_2(SO_4)_3 + Cr_2(SO_4)_3 + 6H_2O$$

$2CrO_3$	$6FeSO_4$	$6H_2SO_4$	$3Fe_2(SO_4)_3$	$Cr_2(SO_4)_3$
chromic acid	ferrous sulfate	sulfuric acid	ferric sulfate	chromic sulfate

for treating chromium wastes, reaction times are on the order of minutes. Additional time is usually allowed to ensure complete mixing and reduction. Once reacted, the reduced solution is then generally subjected to some form of treatment to settle or precipitate the reduced material. A treatment for the removal of what remains of the reducing agent may be included. This can be unused reducing agent or the reducing agent in its oxidized state. Unused alkali metal hydrides are decomposed by the addition of a small quantity of acid. The pH of the reaction medium is typically increased so that the reduced material will precipitate out of solution. Filters or clarifiers are often used to improve separation.

b. <u>Applications</u>.

(1) The principal application of reduction has been chromium treatment and removal. Reduction reactions are typically pH dependent and will-* likely require pH adjustment.

(2) A second application of reduction is the removal of residuals of oxidants such as ozone, chlorine, chlorine dioxide, hydrogen peroxide, etc. Also, any off-gases from ozone generation and application require reduction before discharge to the atmosphere.

(3) Some specialized reduction reactions use hydrogen gas.

c. <u>Advantages/Disadvantages</u>. Advantages/disadvantages of reduction reactions are summarized below:

Advantages	Disadvantages
Reduction can reduce the toxicity of some material	Reduction reactions usually require pH adjustment as pretreatment
Reduction can provide favorable conditions for precipitation of some metals	Can cause the precipitation of some metals

d. Data Requirements. Typical data requirements are listed below:

(1) Influent and peak flow rates.

(2) Variability of influent volumes and concentrations.

(3) pH conditions favorable to reduction reaction.

(4) Concentrations of chemical species that require reduction.

(5) Effectivness of the reducing agent to effect the desired reaction.

(6) Presence of interfering or competing chemicals in the waste.

e. Design Criteria.

(1) If wide fluctuations in flow and concentration are expected, equalization should precede this step.

(2) pH adjustment should be used as a pretreatment step to bring the solution to the desired pH.

(3) A stirred tank should be used to carry out the reduction. A chemical feed system is required to continuously charge the reducing agent. An oxidation reduction potential (ORP) control system may be used to control the quantity of reducing agent added.

(4) Detention time to accomplish chemical reduction will vary from 15 to 45 minutes and will be dictated by the particular reaction involved. Chromium reduction will require approximately 30 minutes but depends upon the pH and reducing agent used.

4-10. Precipitation.

a. Process Description.

(1) Precipitation is a widely used (in industrial practice), relatively low-cost physical chemical technique in which the chemical equilibrium of a waste is changed to reduce the solubility of the undesired components. These components precipitate out of solution as a solid phase, often in the form of small, colloidal particles, and are removed by one of

several possible solids removal techniques. Precipitation is most commonly used to treat heavy-metal-containing wastes.

(2) Precipitation can be induced by one of the following means:

(a) Adding a chemical that will react with the hazardous constituent in solution to form a sparingly soluble compound.

(b) Adding a chemical to cause a shift in solubility equilibrium, reducing the solubility of the hazardous substance.

(c) Changing the temperature of a saturated or nearly saturated solution in the direction of decreased solubility.

(3) Chemical additives are most commonly used. Typical reagents are:

(a) Sodium hydroxide, sodium sulfide.

(b) Hydrated lime ($Ca(OH)_2$).

(c) Iron salts such as iron sulfide, ferric sulfate.

(d) Phosphate salts (especially for heavy metals such as As, Cd, Cr, Zn, Cu, Pb, Hg, Ni).

(e) Alum ($Al_2(SO_4)_3$).

(4) The theoretical removal limit for many metal species is very low, particularly with sulfide precipitants. Figure 4-12 shows theoretical curves as a function of waste pH. Some organic species, for example, aromatic compounds and phthalates, can also be treated. Removal in practice often is one to two orders of magnitude less than the theoretical limit. Complexing agents, such as cyanide or ethylenediamine tetra-acetic acid (EDTA), may compete with the precipitant and hold the species in solution.

(5) Conventional precipitation processes are performed in the following three steps:

(a) Rapid mixing of precipitating chemicals and waste water.

(b) Slow mixing of treated waste water in a flocculation tank to allow settleable flocs to form.

(c) Sedimentation of solids in a clarification tank.

(6) The solids are removed by either:

(a) Sedimentation, which separates the phases by the gravitational settling of the precipitate to the bottom of the sedimentation tank.

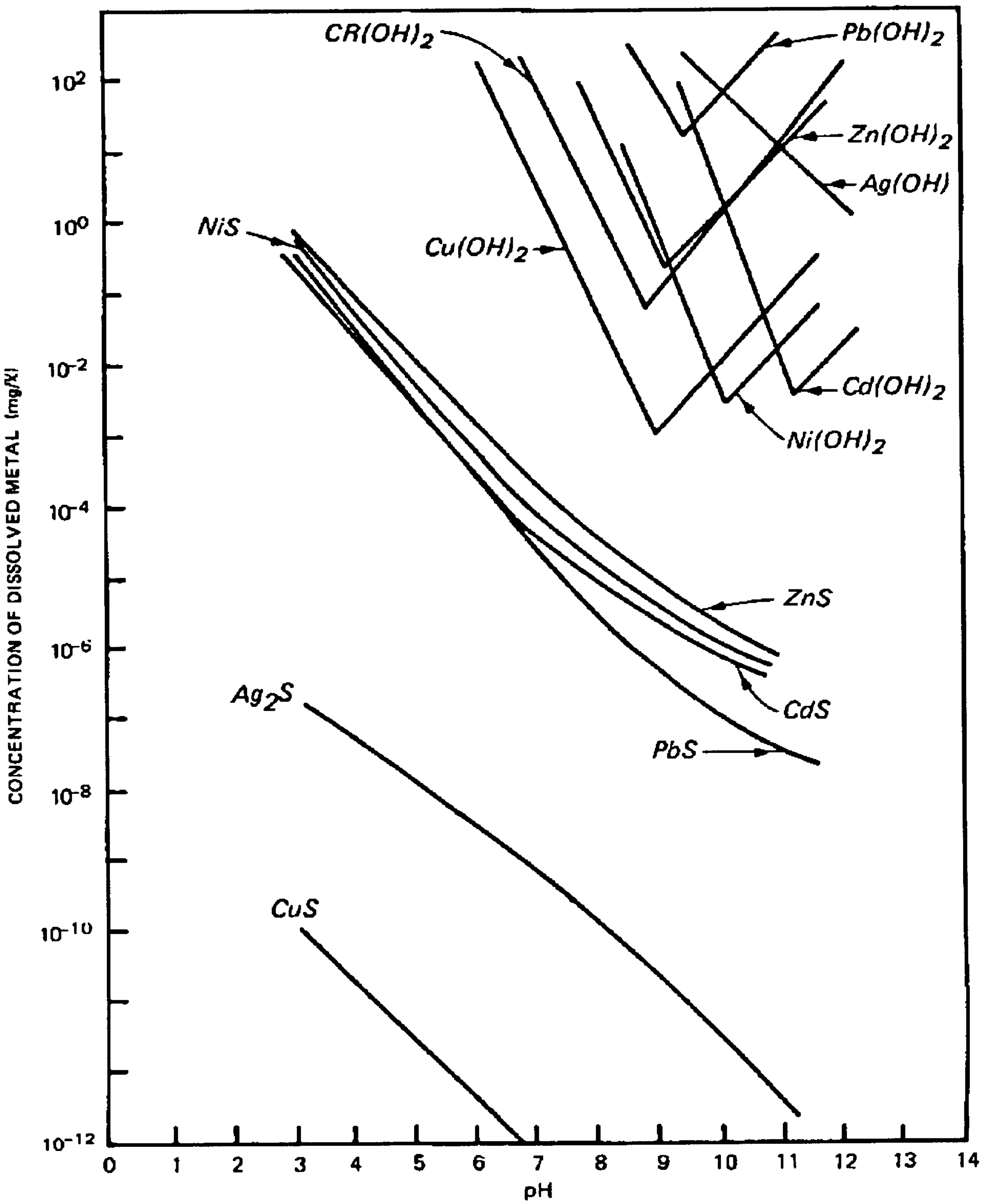


Figure 4-12. Solubility of Metal Hydroxides and Sulfides
(Source: Ghassemi et al. 1981, EPA 1983)

(b) Filtration, which separates the phases by passing the precipitation effluent through a granular or cloth barrier, retaining the particles and allowing the clear effluent to pass through.

(c) Centrifugation, which separates the two phases in an enclosed vessel using centrifugal force to cause the solids to migrate through the liquid.

b. Applications.

(1) Precipitation is a process that finds its primary application in the area of metals removal. However, it may also be used to precipitate long chain or high molecular weight organic materials.

(2) Typically, metals are precipitated as the hydroxide and removed by sedimentation. Removals are limited by the physics of the system. Solubilities of metal sulfides and metal xanthates are much lower than the hydroxide and consequently may be used in situations where very low concentrations are required.

c. Advantages/Disadvantages. The technique of precipitation is widely used for treating waste containing metals. This concept enjoys a technology based upon thermodynamics which provides a theoretical base for the consideration of a multitude of operations. Limitations are also defined by thermodynamics.

(1) The extent of removal is governed by the physics of the system.

(2) High TDS reduces performance, requiring the use of activity coefficients.

(3) Chelating agents can drastically reduce performance.

(4) A variety of anions may be used to improve performance.

(5) Precipitate will usually require a coagulation and/or flocculation step.

d. Data Requirements. In most cases, data will be available in the literature for pure single component systems without interferences. These data should be adequate for planning level design. However, this should be confirmed by bench or pilot plant testing.

e. Design Criteria. Solubility relationships are generally much more complex than indicated in the preceding discussion. In natural waters or waste waters , several other factors must be considered in order to make a realistic solubility product calculation. The ionic strength of the solution affects ion activity and must be considered if more exact calculations are desired.

4-11. Flocculation and Sedimentation. Flocculation and sedimentation are well-developed waste-water treatment processes currently being applied to the full-scale treatment of many industrial waste waters containing particulates and/or soluble heavy metals. The operating parameters and economics associated with the application of flocculation and sedimentation to the treatment of specific industrial waste-water streams are well defined and well documented (refer to CAPDET for design considerations).

a. Process Description.

(1) Historically, the terms "flocculation" and "coagulation" have been used rather indiscriminately and interchangeably to describe the process by which small, unsettleable particles suspended in a liquid medium are made to agglomerate into larger, more settleable particles. For the purpose of this manual, the term "flocculation" shall be defined so as to encompass all of the mechanisms by which suspended particles agglomerate into larger particles. No distinction will be made between coagulation and flocculation.

(2) A variety of mechanisms are involved in the process of flocculation whereby small particles are made to form larger particles. Most of these mechanisms involve surface chemistry and particle charge phenomena. In simple terms, these various phenomena can be grouped into two sequential mechanisms:

(a) Chemically induced destabilization of the repulsive surface-related forces, thus allowing particles to stick together when contact between particles is made.

(b) Chemical bridging and physical enmeshment between the now nonrepelling particles allows for the formation of large particles.

(3) Typical chemicals used to cause flocculation include alum, lime, and various iron salts (ferric chloride, ferrous sulfate). Organic flocculating agents, often referred to as "polyelectrolytes," have come into widespread use. These materials generally consist of long-chain water-soluble polymers such as polyacrylamides. They are used either in conjunction with the inorganic flocculants such as alum or as the primary flocculating agent alone.

(4) The inorganic flocculants, such as alum, lime, or iron salts, make use of precipitation reactions. Alum (hydrated aluminum sulfate) is typically added to aqueous waste streams as a solution. Upon mixing, the slightly higher pH of the water causes the alum to hydrolyze and form fluffy, gelatinous precipitates of aluminum hydroxide. These precipitates, partially due to their large surface area, act to enmesh small particles and thereby cause larger particles. Lime and iron salts, as well as alum, are used as flocculants primarily because of this tendency to form large fluffy precipitates or "floc" particles. Many precipitation reactions, such as the precipitation of metals from solution by the addition of sulfide ions, do not readily form floc particles, but rather precipitate as very fine and relatively stable colloidal particles. In such cases, flocculating agents such as alum and/or polyelectrolytes must be added to cause flocculation of the metal sulfide precipitates.

(5) In the flocculation process, it is essential that the slow mixing step be very gentle and be given sufficient time, as newly agglomerated particles are quite fragile and can be broken apart by shear forces during mixing. Once suspended particles have been flocculated into larger particles, they can usually be removed from the liquid by sedimentation, provided, of course, that a sufficient density difference exists between the suspended matter and the liquid.

(6) Sedimentation is a purely physical process whereby particles suspended in a liquid are made to settle by means of gravitational and inertial forces acting on both the particles suspended in the liquid and the liquid itself. The fundamental elements of most sedimentation processes are:

(a) A basin or container of sufficient size to maintain the liquid to be treated in a relatively quiescent state for a specified period of time.

(b) A means of directing the liquid to be treated into the above basin in a manner which is conducive to settling.

(c) A means of physically removing the settled particles from the liquid (or the liquid from the settled particles, whichever the case may be).

(7) Clarifiers are gravity separation devices and are usually the type of equipment used in applications that involve precipitation and flocculation in addition to sedimentation. Very often, all three processes take place within the same piece of equipment (clariflocculator) since many clarifiers are equipped with separate zones for chemical mixing and precipitation, flocculation, and settling. Certain clarifiers are equipped with low lift turbines which mix a portion of the previously settled precipitates with the incoming feed, as this practice has been shown to enhance certain precipitation reactions and promote favorable particle growth. (This type of clarifier is often used in water-softening applications involving the precipitation of calcium as calcium carbonate.)

b. Applications. The processes of flocculation and sedimentation are suitable treatment methods whenever it is necessary to remove suspended particulates and/or soluble heavy metals. The most common applications suitable for hazardous waste sites will include:

(1) Settling of suspended solids from surface water run-off.

(2) Removal of soluble and insoluble toxic metals.

(3) Removal of soluble inorganics natural to ground-water supplies.

Many toxic metals, including cadmium, lead, arsenic, and chromium, are removed to some degree from waste waters by these processes. There is no upper limit on the concentrations that can be treated by these processes. The lower limit for removal of soluble species is generally governed by the solubility product of the particular ion, although this method of predicting removal efficiency is not very reliable.

c. Advantages/Disadvantages. The major advantages and disadvantages of flocculation and sedimentation as applied to hazardous waste sites are summarized below:

Advantages	Disadvantages
Can be economically applied to very large volumes of leachate or ground water	Often yields incomplete removal of many hazardous compounds
Widely used, equipment is relatively simple	Large quantities of hazardous sludges may be generated
Very low energy consumption	Equipment may be difficult to obtain for flows of less than 37.9 m^3/day (-10,000 gpd)
No upper limit to concentrations that can be treated	Because of continually changing leachate quality, required dosages of coagulants will continuously change

d. Data Requirements.

(1) The required dosage of coagulant depends upon pH, alkalinity, phosphate levels, and mode of mixing; dosage can be determined by jar tests and zeta potential tests. Typical chemical dosages used in industrial treatment processes are listed in Table 4-15. The hydraulic loading, also listed in Table 4-15, is used as a basis for determining suspended solids removal efficiencies. The hydraulic loadings shown are intended to achieve 80 to 90 percent suspended solids removal.

Table 4-15. Chemical Treatment of Industrial Waste Water by Coagulation

Criteria	$FeCl_3$	Alum	$Ca(OH)_2$
Dose, mg/ℓ	80-120	100-150	350-500
Hydraulic loading, $m^3/m/m^2$ (gpm/sq ft[1])	1.2×10^{-3} to 1.6×10^{-3} (0.3-0.4)	8.2×10^{-4} to 1.6×10^{-3} (0.2-0.4)	2×10^{-3} to 3.3×10^{-3} (0.5-0.8)
Chemical sludge production, mg/ℓ (lb/million gal)	42-84 (350-700)	30-60 (250-500)	480-839 (4,000-7,000)

[1]Without use of polyelectrolytes.

(2) Other data required to size the settling basins will include:

(a) Waste stream daily and peak flows.

(b) Settling velocity.

(c) Waste stream analysis for size distribution and solids and liquid specific gravity.

e. Design Criteria.

(1) The effectiveness of a particular flocculant varies in different applications, and in a given application each flocculant has an optimum concentration and pH range. The process of flocculation requires rapid mixing followed by a slow and gentle mixing to allow contact between small particles and agglomeration into larger particles. Rapid mixing for coagulants especially inorganic coagulants such as alum is required to completely disperse the coagulant into the water immediately. Rapid mixing is usually accomplished in 10 to 60 seconds. A mean temporal velocity gradient in excess of 91 m/s (300 feet per second per foot) is recommended. After achieving an effective mix, promotion of particle growth by flocculation during the slow mix step is next. Flocculation is accomplished in 15 to 30 minutes with a mean temporal velocity gradient of 40 to 80 meters per second per meter (40 to 80 feet per second per foot). The lower value is for fragile floc (aluminum or iron), and the higher value is for a lime floc (Azad 1976).

(2) Sedimentation may be carried out in a separate basin from flocculation or it may be carried out in the same basin with both flocculation and precipitation. Figures 4-13 and 4-14 present schematics of an “in-line” system and a sludge-blanket type unit in which all three processes are carried out in a single unit. Criteria for sizing settling basins are overflow rate (surface settling rate), tank depth at the side walls, detention time which usually averages 1 to 3 hours, and surface loading rates which average 1.5 to 2.5 $m^3/d/m^2$ (360 to 600 gallons per day per square foot) for alum floc, 2.2 to 4.9 $m^3/d/m^2$ (540 to 1,200 gallons per day per square foot) for lime floc, and 2.9 to 3.3 $m^3/d/m^2$ (700 to 800 gallons per day per square foot) for $FeCl_3$. In selecting the particular tank shape, proportions, equipment, etc., the designer should:

(a) Provide for even inlet flow distribution in a manner that minimizes inlet velocities and short-circuiting.

(b) Minimize outlet currents and their effects by limiting weir loadings and by proper weir placement.

(c) Provide sufficient sludge storage depths to permit desired thickening of sludge. Solids concentrations of two to seven percent should be obtained.

(d) Provide sufficient wall height to give a minimum of 457 mm (18 inches) of freeboard.

(e) Reduce wind effects on open tanks by providing wind screens and by limiting fetch of wind on tank surface with baffles, weirs, or launders.

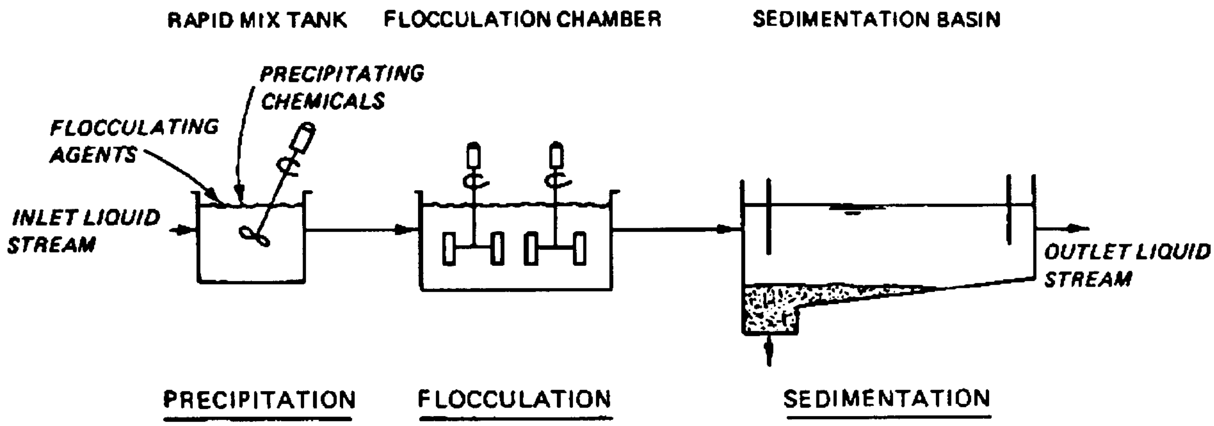


Figure 4-13. Representative Configuration Employing Precipitation, Flocculation, and Sedimentation

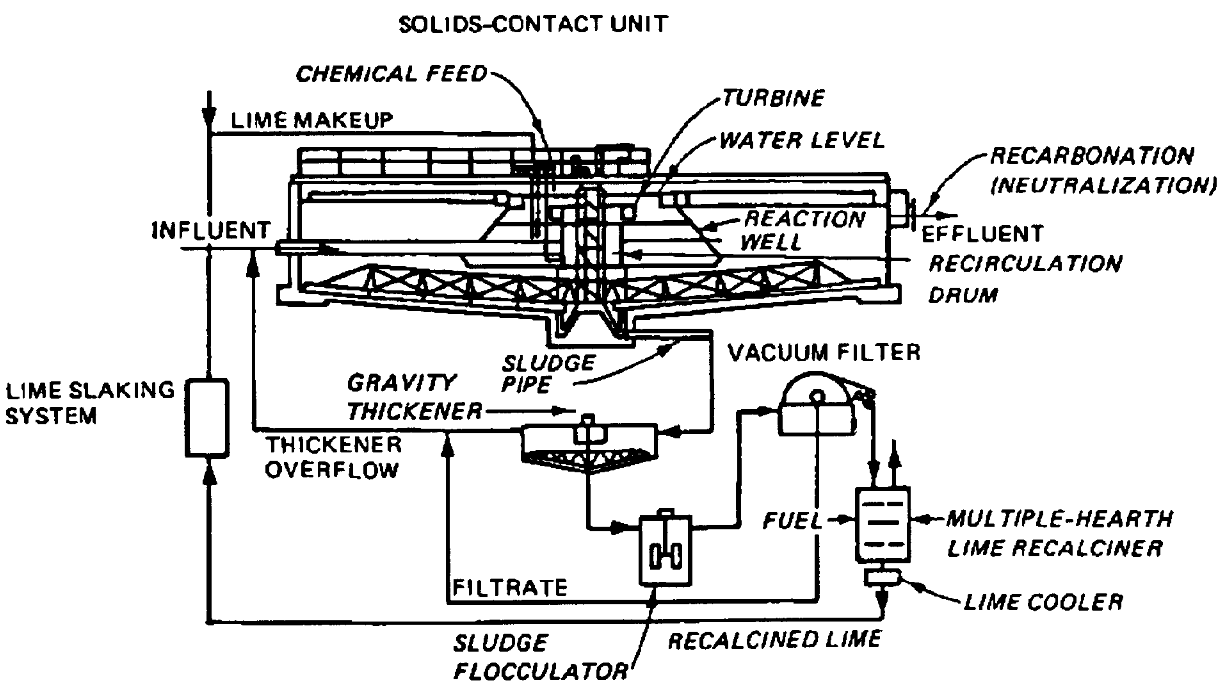


Figure 4-14. Typical Solids Contact Chemical Treatment System

(f) Consider economy of alternative layouts that can be expected to provide equivalent performance.

(g) Maintain equal flow to parallel units. This is most important and often forgotten. Equal flow distribution between settling units is generally obtained by designing equal resistances into parallel inlet flow ports or by flow splitting in symmetrical weir chambers.

4-12. Neutralization.

a. Process Description.

(1) The neutralization process described herein is intended for use in two different ways. The word “neutralization” implies a neutral pH of 7.0. However, in the present context, the process will be used to describe the adjustment and control of pH at a specified level.

(2) Many manufacturing processes generate waste streams that are acidic or alkaline in nature. Before such wastes can be discharged to the environment, the pH must be adjusted to be within the EPA-specified range, usually 6 to 9.

(3) Adjustment of pH may also be desirable to control chemical reaction rates and to effect precipitation. For example, in the reduction of chromium (VI) to chromium (III), the pH must be lowered to 3.0 or less in order for the reaction to proceed at a satisfactory rate. In order to precipitate the chromium (III), the pH must be raised to between 8 to 8.5.

(4) The basic principle behind the process is simple: the mixing of an acid or a base with a process stream to bring about the desired pH. Typically, the process is carried out in a completely stirred reactor (CSTR).

(5) The addition of appropriate quantities of neutralizing agent is monitored and adjusted by pH measurements and control. Generally, these systems are of a continuous flow variety and use automatic pH monitors to check the acidity or alkalinity and control the feeding of neutralizing agent. The number of neutralization units and the location of pH sensors are determined by the stability of the waste stream pH. Where widely varying pH levels are experienced, several reaction units plus additional monitoring equipment may be required. A stream with large fluctuations in pH might also be preceded by an equilization basin which would yield a more consistent feed with a limited pH range.

(6) The choice of a neutralizing agent is dictated by a number of factors such as economics, availability, and process compatibility. Commonly, the choice of an acid for neutralizing alkaline waste is sulfuric acid, whereas the choice for an acid stream may be lime or caustic.

b. Applications. Neutralization is a treatment process of demonstrated technical and economic feasibility industry wide. Two primary applications are intended here and are as follows:

(1) Neutralize a waste stream to a suitable level such that it can be discharged to the environment.

(2) Adjust pH of a waste stream to a specified level that would be suitable for carrying out chemical reactions or further treatment.

c. Advantages/Disadvantages. Advantages and disadvantages of neutralization are summarized below:

Advantages	Disadvantages
Proven and simple process	Does not remove or degrade pollutants, rather adds them
Some waste may be discharged directly following neutralization	pH controllers require frequent maintenance
Can provide favorable conditions for oxidation/reduction reactions	May require equilization as pretreatment
Can provide conditions favorable to precipitation of metals	May generate large amounts of heat

d. Data Requirements. Data requirements include:

(1) Average daily flow; peak flow.

(2) pH range of influent stream.

(3) Desired control pH.

(4) Equivalents per liter of alkalinity or acidity to be neutralized.

e. Design Criteria.

(1) If the influent hydraulic flow is expected to vary significantly, equalization should be considered for pretreatment. This approach is also true for wide fluctuations in the influent pH.

(2) A CSTR with 10 to 20 minutes residence time should suffice in most cases. Neutralization reactions are typically very fast. There may be, however, extenuating circumstances that would make it desirable to increase or decrease this time. A larger volume would tend to stabilize the control system. On the other hand, if pH adjustment is being carried out in a number of stages, retention time may be reduced to a minimum.

(3) Feed systems and storage tanks must be provided for acid and/or base for neutralization. If lime is used, a slurry tank may be required.

(4) If strong acids require neutralization with strong bases, care must be exercised to consider the potential for a violent exothermic reaction. This situation should be avoided if at all possible.

4-13. Oil-Water Separation.

a. Process Description.

(1) Oil-water separators may be of several different types that utilize either gravity or mechanical acceleration to separate phases of varying density. Gravity separators are more commonly called API (American Petroleum Institute) separators. This terminology stems from a hydrometer scale in °API that is used by the petroleum industry to specify the specific gravity of petroleum products.

(2) An API separator consists of a settling chamber that allows oil to separate from an aqueous phase and rise to the surface, a baffle and oil skimming device that prevents the loss of the oil phase to the effluent while continuously removing the surface oil, and a holding basin that collects and stores the oil until final disposal is desired.

(3) Gravity separators should be used only for gross oil-water separators. They are not intended for removals to low parts per million levels. Also, they should not be used for emulsified oil and grease.

(4) Low-level oil removal may require a membrane process, centrifugation, chemical coagulation, or carbon adsorption. One or more of these processes may be used after the API separator. A flow diagram for an API separator is presented in Figure 4-15.

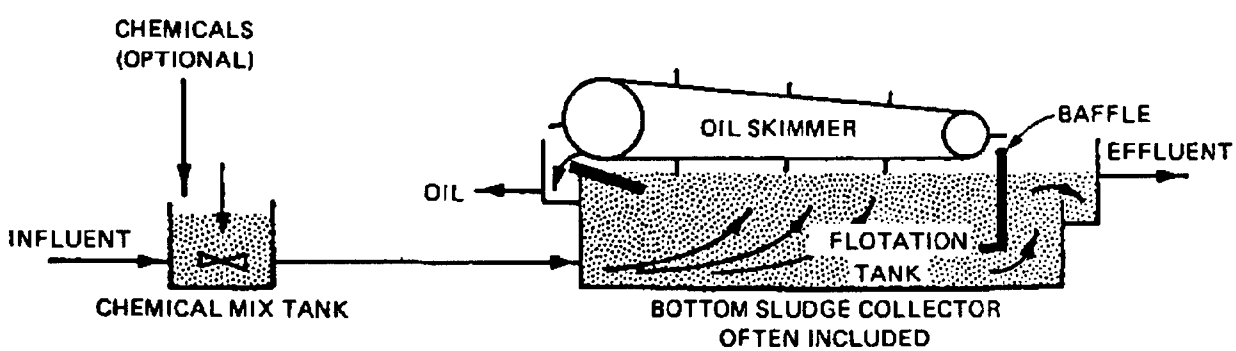


Figure 4-15. Flow Diagram for API Separator

b. Application.

(1) API are gravity separators which are technically simple oil-water separators that have found wide usage at manufacturing facilities. They are used to separate residual oil from washing down floors, equipment, parts, compressor blowdown, and spillage.

(2) Gravity separators are typically used as a pretreatment step before further processing of the waste water. Oil is automatically skimmed and collected in a holding basin where it is held for final disposition. Residual oil in the effluent may be removed in subsequent treatment steps, or specific processes may be required in the process train for total removal, perhaps carbon adsorption.

c. Advantages/Disadvantages. Advantages and disadvantages of oil/water separators are summarized below:

Advantages	Disadvantages
Provide excellent gross oil removal	Cannot treat emulsified oil or oil droplets smaller than 0.015 centimeters
Proven, inexpensive technology	Separated oil requires disposal and water phase may requre futher treatment
Variety of proprietary units are readily available	Short-circuiting may be a problem
	Sensitive to shock loadings

d. Data Requirements. Data requirements are as follows:

(1) Hydraulic flow, average and peak.

(2) Size of oil droplet to be removed.

(3) API or density of oil.

(4) API or density of water phase.

(5) Viscosity of fluid.

(6) Expected operating temperature.

e. Design Criteria.

(1) Gravity separators are based upon the rise rate of oil droplets of a specified size and density. These droplets rise to the surface or to a baffle and then to the surface within the retention time provided. A skimming device then physically removes the oil to a holding facility.

(2) Rise rates are amenable to theoretical considerations through a rather simple force balance on the system. These forces include drag, buoyant, and gravitation forces. The design of oil separators as developed by the American Petroleum Institute is based upon removing oil droplets that are larger than 0.015 centimeter in diameter. The Reynolds number for this situation can be shown to be less than 0.5. This says that, for spherical

particles, laminar flow can be assumed with little error and Stoke*s law is applicable.

(3) Stoke*s law describes the terminal settling velocity of a particle as a function of the particle and medium density, particle diameter, and drag characteristics. Stokes equation is as follows:

$$V_t = \frac{(P_s - P)\, g D_p^2}{18u} \qquad (4\text{-}5)$$

where

V_t = terminal settling velocity, cm/sec

P_s = density of particle, g/cm^3

P = density of fluid, g/cm^3

g = gravitational constant, cm/sec^2

D_p = diameter of particle, cm

u = viscosity of fluid, dyne-sec/cm^2

(4) The API design procedure must consider short-circuiting and turbulence for best performance.

4-14. Dissolved Air Flotation.

a. Process Description.

(1) Flotation is a solid-liquid separation process. Separation is artificially induced by introducing fine gas bubbles (usually air) into the system. The gas-solid aggregate has an overall bulk density less than the density of the liquid; thus, these aggregates rise to the surface of the fluid. Once the solid particles have been floated to the surface, they can be collected by a skimming operation.

(2) Air flotation systems may be classified as dispersed air flotation or dissolved air flotation. In dispersed air flotation, air bubbles are generated by introducing air through a revolving impeller or porous media. This type of flotation system is usually ineffective and finds very limited application in waste-water treatment. Dissolved air flotation may be subclassified as pressure flotation or vacuum flotation. Pressure flotation involves air being dissolved into the waste water under elevated pressures and later released at atmospheric pressure. Vacuum flotation consists of applying a vacuum to waste water aerated at atmospheric pressure. Dissolved air-pressure flotation considered herein is the most commonly used in waste-water treatment.

(3) The principal components of a dissolved air-pressure flotation system are a pressurizing pump, air injection facilities, a retention tank, a back-pressure regulating device, and a flotation unit. The primary variables for flotation design are pressure, recycle ratio, feed solid concentration, detention period, air-to-solids ratio, use of polymers, and solids and hydraulic loadings. Optimum design parameters must be obtained from bench scale or pilot plant studies. A flow diagram for a dissolved air flotation system is presented in Figure 4-16.

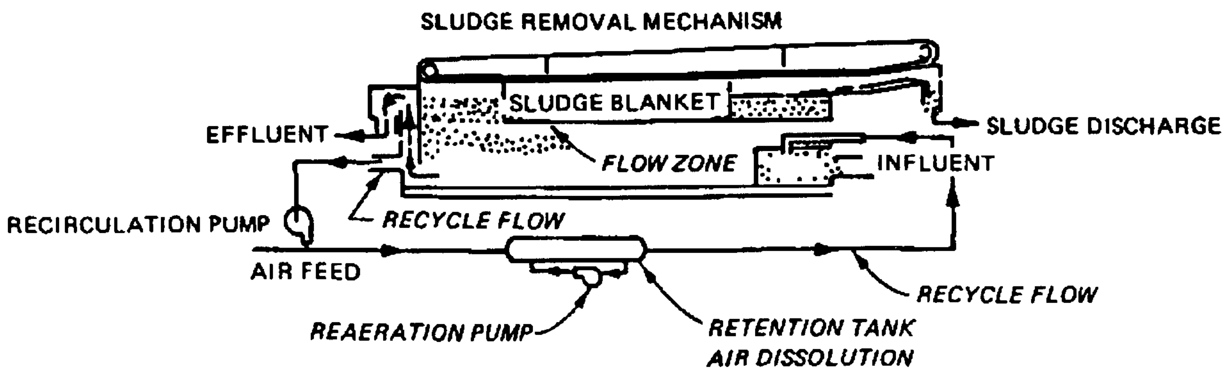


Figure 4-16. Flow Diagram for Dissolved Air Flotation System

b. Applications. In waste-water treatment, flotation is used as a clarification process to remove suspended solids and as a thickening process to concentrate various types of sludges. However, high operating costs of the process generally limit its use to clarification of certain industrial wastes and for concentration of waste-activated sludge. In industrial practice, with wastes containing total suspended solids (TSS) and oil and grease levels up to 900 milligrams per liter, removal efficiency of 90 percent has been recorded.

c. Advantages/Disadvantages. Advantages and disadvantages of dissolved air flotation are summarized below:

Advantages	Disadvantages
Requires very little land area	Only effective on particles with densities near that of water
Well documented and available technology	Varying influent will affect performance
	Sludge generated will require disposal
Air released in unit unlikely to strip volatile organics	

d. Data Requirements. Required design information includes:

(1) Waste stream daily average flow.

(2) Waste stream temperature.

(3) Waste stream oil/grease or suspended solids concentration.

(4) Treatability tests to determine air requirements and pressure.

e. Design Criteria.

(1) Major design variables and corresponding operating conditions are:

(a) System pressure, 276-413 kPa (40-60 psig) (pounds per square inch, gage).

$$\frac{A}{S} = \frac{1.3s_a(fP - 1)}{S_a}$$

Temp., °C	0	10	20	30
s_a, mℓ/ℓ	29.2	22.8	18.7	15.7

where

A/S = air to solids ratio, mℓ (air)/mg (solids)

S_a = air solubility, mℓ/ℓ

f = fraction of air dissolved at pressure P, usually 0.5

P = pressure, atm

$$= \frac{p + 14.7}{14.7} \quad \text{(U.S. customary units)}$$

$$= \frac{p + 101.35}{101.35} \quad \text{(SI units)}$$

p = gage pressure, lb/in^2 gage (kPa)

S_a = sludge solids, mg/ℓ

The corresponding equation for a system with only pressurized recycle is

$$\frac{A}{S} = \frac{1.3s_a(fP - 1)R}{S_aQ}$$

where

R = pressurized recycle, Mgal/d (m^3/d)
Q = mixed-liquor flow, Mgal/d (m^3/d)

In both equations, the numerator represents the weight of air and the denominator the weight of the solids. The factor 1.3 is the weight in milligrams of 1 mℓ of air, and the term (-1) within the brackets accounts for the fact that the system is to be operated at atmospheric conditions. The required area of the thickener is determined from a consideration of the rise velocity of the solids, 0.2 to 4.0 gal/m • ft^2 (8 to 160 ℓ/m^2 • min), depending on the solids concentration, the degree of thickening to be achieved, and the solids-loading rate.

(b) Hydraulic loading, 4.1×10^{-3} - 1.6×10^{-2} $m^3/min/m^2$ (1-4 gpm/ft^2).

(c) Retention period, 20-40 mm.

(2) It is common engineering practice to triple the calculated A to provide a safety factor and excess air for high dissolution efficiency.

(3) The hydraulic loading rate (referred to as surface loading rate (SLR)) is determined by plotting laboratory experimental values of effluent pollutant concentrations versus surface loading rates. The rate which is sufficient to achieve effluent water quality goals is identified from the graph.

(4) The retention time equation is

$$t = \frac{d}{SLR} \qquad (4\text{-}7)$$

where a depth of 1.2 to 2.7 m (4 to 9 feet) is typically chosen (EPA 1980).

4-15. <u>Reverse Osmosis</u>.

a. <u>Process Description</u>.

(1) Osmosis is the movement of a solvent through a membrane which is impermeable to a solute. If a salt solution is separated from water by means of a semipermeable membrane, there will be a net transport of water in the direction of the salt solution. This phenomenon develops a hydrostatic pressure known as “osmotic pressure.” It may also be defined as the excess pressure that must be applied to the solution to produce equilibrium.

(2) Reverse osmosis removes contaminants from aqueous wastes by passing the waste stream, at high pressure, through a semipermeable membrane. At sufficiently high pressure, usually in the range of 1378 to 2756 kPa (200 to 400 pounds per square inch), pure water passes out through the membrane leaving a more concentrated waste stream. As the waste stream becomes more concentrated, the osmotic pressure increases and consequently requires addi-

tional external pressure to maintain the flow in the proper direction, hence the name reverse osmosis.

(3) The semipermeable membrane itself is perhaps the most critical part of reverse osmosis (RO). At present, commercial RO membranes are made from two types of polymers. The first membranes developed were cellulose acetate. The second type of membranes were developed from cellulose triacetate. Both membranes can be prepared in sheet form with water fluxes of 4.1×10^{-2} -8.2×10^{-2} $m^3/day/m^2$ (10 to 20 gallons per day per square foot) at 2756 kPa (400 pounds per square inch). Polyamine membranes are being developed but, at present, they have no resistance to chlorine.

(4) The design of the modules containing the RO membranes is crucial to the efficient operation of the process. As solute is rejected by the membranes, it concentrates at the membrane surface and results in a situation known as "concentration polarization," where the concentration at the membrane surface is many times higher than in the bulk feed solution. Since the driving force for water transport decreases with increasing concentration, polarization can have a very deleterious effect on water flux.

(5) Concentration polarization can be minimized by high fluid shear at the membrane surface to aid the back-transport of polarized solute into the bulk of the process stream. This is accomplished by flowing the feed stream at high velocities in thin channels to promote laminar shear, or in wide channels to produce turbulence. RO membranes can be spiral wound, hollow fine fiber, tubular, or flat membrane.

(6) One of the difficulties with RO membranes is their susceptibility to fouling by film-forming organics or insoluble salts. It is common practice to preprocess feed water as necessary to remove oxidizing materials, iron, and magnesium salts; to filter out particulates; and to remove oils, greases, and other film-formers. If there is likelihood of fouling by living organisms, chlorination or UV treatment may be employed as well to ensure that maximum flux rates may be obtained. A typical flow sheet for an RO plant is shown in Figure 4-17.

b. Applications.

(1) RO systems are in extensive use throughout the world in generating potable water. Over 2.27×10^5 m^3/day (60,000,000 gallons per day) in capacity is now in operation.

(2) The number of plants in use to treat industrial waste water is not clearly defined but appears to be significant. Specific applications include:

(a) Preparation of pure water and process feed water.

(b) Preparation of rinse water in semiconductor and electronic manufacturing.

(c) Purification of water for hospital use.

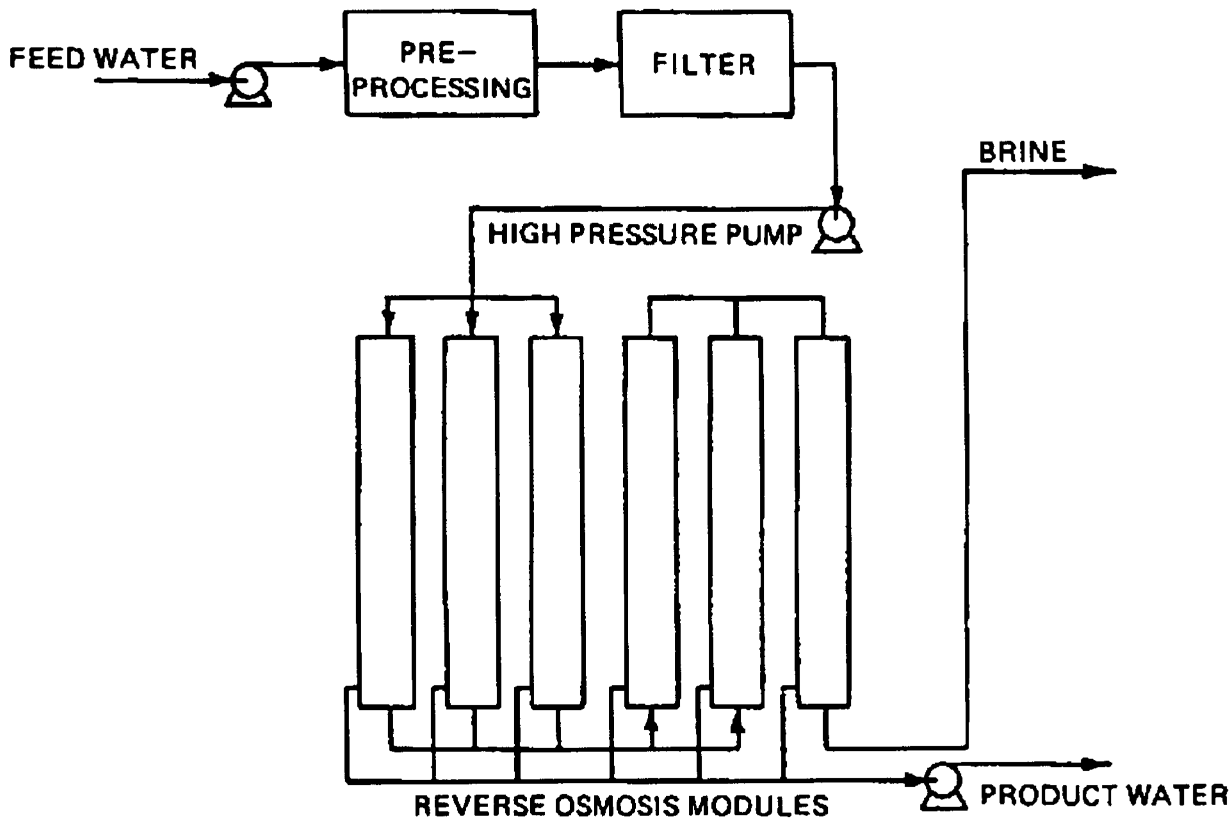


Figure 4-17. Reverse Osmosis Plant Flow Sheet

(d) Reclamation of electroplating chemicals.

(e) Recovery of sugar wastes by candy manufacturers.

(3) Industrial waste treatment offers a great potential for RO. This process should be considered when it is desirable or necessary to accomplish:

(a) A reduction in the waste volume.

(b) Recovery of valuable or reusable materials.

(c) Water conservation and recovery.

(d) The concentration of pollutants for further processing.

c. Advantages/Disadvantages. Advantages and disadvantages of reverse osmosis are listed below:

Advantages	Disadvantages
Capable of high salt rejection	Requires high operating pressure and extensive pretreatment
Produces high purity solvent	Subject to membrane fouling and compression
Applicable to small installations	Cannot be used for fractionation
Provides for water conservation and use	Proportion of reject water may be too high to be acceptable

d. Data Requirements.

(1) A variety of proprietary designs for RO units are available from numerous manufacturers. These suppliers will usually supply the following pertinent information with regard to their particular system and for a variety of membranes:

(a) Packing density, m^2/m^3 (ft^2/ft^3).

(b) Water flux at a specified pressure and temperature.

(c) Sodium chloride rejection.

(d) Acceptable pH ranges.

(e) Recommended operating pressure.

(2) Data with regard to specific waste are also required that must be determined experimentally from bench scale studies. Manufacturers and suppliers are usually eager to be of help in this area.

(3) One important piece of information that must be determined for any specific application is pretreatment requirements. In general, pretreatment will always be required and should be carried out to:

(a) Remove excess turbidity and suspended solids.

(b) Adjust pH to desirable level.

(c) Adjust temperature of feed.

(d) Control the formation of components that tend to precipitate.

(e) Disinfect to prevent slime growth.

(f) Remove oil and grease that may be present.

(4) Data regarding flux rates must be determined experimentally. Flux decline is a serious operational problem that must be given the proper attention. Membrane compaction and membrane fouling are responsible for reductions in flux. Membrane compaction is a function of membrane type, operating temperature, pressure, and time.

e. Design Criteria.

(1) The design of an RO system is based upon the feed water composition, variability, temperature, and osmotic pressure. Rejection of various components in the feed stream by a specific membrane flow rate usually dictates the number of units or size of the plant. Product quality is difficult to predict but can be varied by adjusting product recovery.

(2) When plant capacity and energy requirements are established, the membrane requirements must be set. Membrane considerations include the expectancy, compaction, fouling, and operating net pressure. If, for example, data are available for a certain membrane that would suggest a flux of 10 gallons per square foot per day at 70°F at 500 pounds per square inch is applicable, the membrane requirement for a 100,000 gallons-per-day facility would be 10,000 square feet of membrane. It is common design practice to base the design flux upon the expected volume after 1 year of operation which may reduce flux rate by 10-15 percent. Membrane lifetime is critical.

(3) Minimization of concentration polarization is another design consideration. This is done by regulating the brine flow rate through the RO units. Since product is continuously being taken out, the brine flow is reduced. To compensate for this, units are staged in a series-parallel arrangement that is similar to an inverted pyramid.

4-16. Solidification/Stabilization. Solidification/stabilization technology as applied to wastes uses physical and chemical processes to produce chemically stable solids with improved contaminant containment and handling characteristics. Waste solidification is the term used to describe the process of sorbing a liquid or semiliquid waste onto a solid medium, such as fly ash, cement, kiln dust, or clay, or otherwise incorporating the waste in a solid matrix. This partial treatment eliminates any free liquid and reduces the risk of spillage or escape of contaminants in any liquid phase. This technology is discussed in detail in paragraph 4-21.

4-17. Ultrafiltration.

a. Process Description.

(1) Ultrafiltration and RO are similar processes and some confusion exists about their distinction. Both involve the transport of a solution under a pressure gradient through a semipermeable membrane to achieve at least partial separation of solvent molecules from solute molecules. In addition, both require a velocity vector parallel to the plane of filtration. The two processes differ because ultrafiltration is not impeded by osmotic pressure and can be effected at low pressure differences of 34.5 to 689 kPa (5 to 100 pounds per square inch). Ultrafiltration is usually applicable for separation

of solutes above a molecular weight of 500, which have very small osmotic pressures at moderate concentrations. These include such materials as bacteria, viruses, starches, gums, proteins, clays, and paint pigments. The upper molecular weight limit for ultrafiltration is usually defined as 500,000. Above that molecular weight size, separation occurs by conventional microporous filtrations.

(2) Concentration polarization effects in ultrafiltration are similar to those in RO except more severe. Since micromolecular diffusion constants are two to three orders of magnitude smaller than those of salts, back-diffusion to the bulk of the liquid is much slower. Figure 4-18 illustrates the impact of concentration polarization.

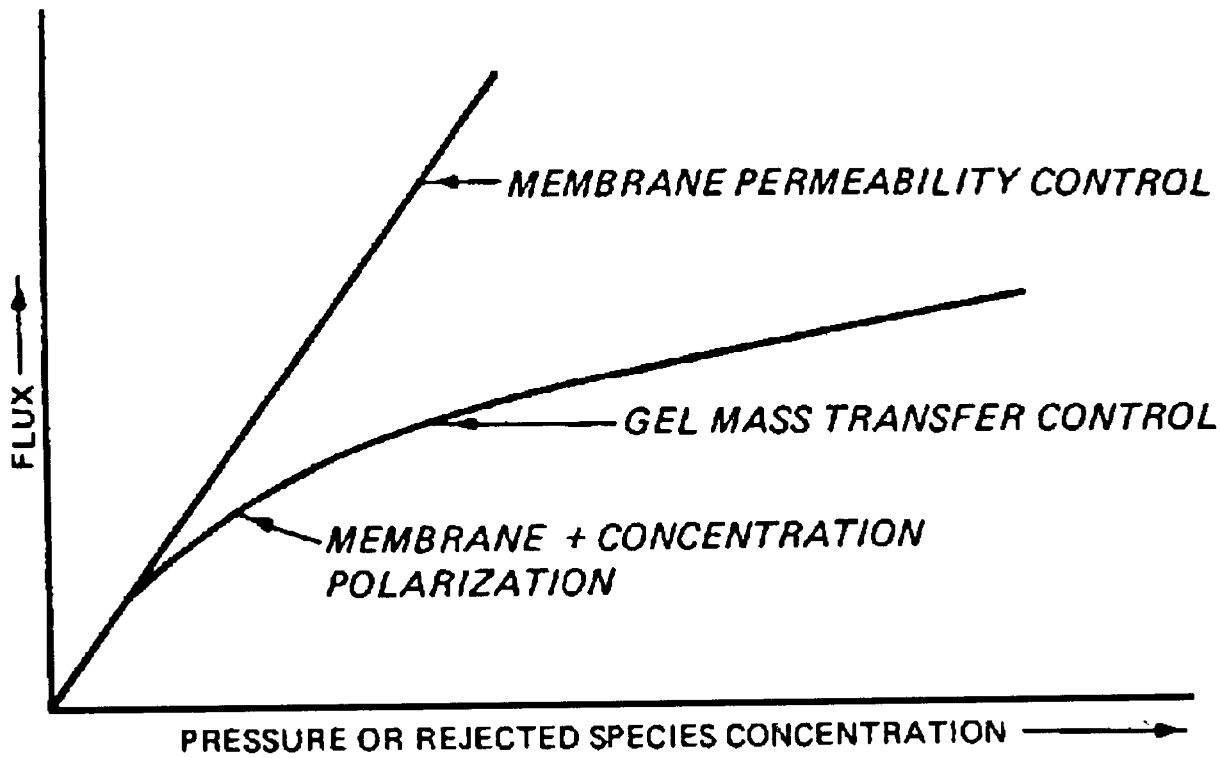


Figure 4-18. Effect of Concentration Polarization Upon Membrane Flux in Ultrafiltration

b. <u>Applications</u>.

(1) The properties of ultrafiltration membranes lead to a range of applications quite distinct from those of conventional filtrations. Where solutes are being separated from solution, ultrafiltration can serve as a concentration or fractionation process for single-phase liquid streams. Thus, ultrafiltration competes with adsorptive and evaporative separation processes and has the potential for broader applicability than conventional filtration. Usually, it will not perform the entire task because it produces a concentrate

rather than a solvent-free product, and the concentrate requires further processing if a pure solute is to be recovered.

(2) Application of ultrafiltration may fall into one of three categories:

(a) Concentration, where the desired component is rejected by the membrane and taken off as a fluid concentrate.

(b) Fractionation, for systems where more than one solute is to be recovered, and products are taken from both the rejected concentrate and permeate.

(c) Purification, where the desired product is purified solvent.

(3) Table 4-16 summarizes major existing ultrafiltration applications. Also shown is the function of ultrafiltration processing for the specific application.

(4) Table 4-17 summarizes developmental applications of ultrafiltration. These represent areas which are likely to be commercial within the next 5 years. Table 4-16 indicates commercial applications and the nature of their technology.

Table 4-16. Commercial Applications of Ultrafiltration

Application	Function
Electrocoat	Fractionation
Paint rejuvenation and rinse water	Concentration and fractionation
Protein recovery from cheese whey	Concentration and fractionation
Metal machining, rolling, and drawing--oil	Purification
Emulsion treatment	Purification
Textile sizing (PVA) waste	Fractionation
Electronics component manufacturing washwater treatment	Purification
Pharmaceuticals manufacturing sterile water production	Purification

c. Advantages/Disadvantages. Ultrafiltration is a concentration process that is in competition with other membrane processes as well as evaporation processes. Its advantages and disadvantages are summarized below:

Advantages	Disadvantages
Operates at lower pressure than RO	Requires membranes that are subject to fouling
Can be used for fractionation	Limited range of particle sizes for for which it is effective
Does not require pretreatment as RO, but can be used as pretreatment for RO	
Requires less capital than RO or evaporative processes	
Highly suitable for small flows and small installations	

Table 4-17. Development Applications of Ultrafiltration

Application	Function
Dye waste treatment	Concentration and purification
Pulp mill waste treatment	Concentration and purification
Industrial laundry waste treatment	Purification and fractionation
Protein recovery from soy whey	Concentration
Hot alkaline cleaner treatment	Fractionation and purification
Power plant boiler feedwater treatment	Purification
Sugar recovery from orange juice pulp	Fractionation
Product recovery in pharmaceutical and fermentation industries	Concentration
Colloid-free water pollution for beverages	Purification

d. Data Requirements.

(1) A variety of proprietary designs for ultrafiltration units are available from numerous manufacturers. These suppliers will usually supply the following pertinent information with regard to their particular system and for a variety of membranes:

(a) Packing density, 1.5 m^2/m^3 (5 ft^2/ft^3).

(b) Water flux at a specified pressure and temperature.

(c) Molecular weight cutoff or rejection.

(d) Acceptable pH ranges.

(e) Recommended operating pressure.

(2) Data with regard to specific waste are also required that must be determined or verified experimentally. Manufacturers and suppliers will usually provide assistance in this area. Flux rates and rejection should be determined experimentally.

e. Design Criteria.

(1) The approach to the design of an ultrafiltration system is similar to that for RO. In ultrafiltration design, concentration polarization effects are magnified, and care must be exercised to alleviate this problem. Typically, channels are designed for minimum height, and the unit is operated at a high parallel surface velocity.

(2) Operating pressures for ultrafiltration systems are in the range of 68.9 to 689 kPa (10 to 100 pounds per square inch) with 413 to 551 kPa (60 to 80 pounds per square inch) being typical. As is the case with RO, temperature plays a significant role in the flux rate of ultrafiltration membranes. Fluxes are expected to double for a 15° to 25°C rise in temperature. Operating temperatures are limited by economics and the material from which the membrane is constructed. Membranes produced from cellulose are limited to the 50° to 60°C range, while other membranes may be operated at temperatures as high as 100°C.

(3) Ultrafiltration membranes are specified in terms of molecular weight cutoff or a rejection of a specific molecular weight compound. This is not an absolute measure of rejection. In actuality, rejection is a function of molecular shape, size, and flexibility as well as the operating conditions.

Section II. Treatment of Sludges and Soils

4-18. Biological Treatment.

a. Bioslurry Reactors.

(1) Process description.

(a) Bioslurry reactors (BSRs) (also referred to as liquid/solids reactors) are an innovative biological technology for rapid treatment of sludges and excavated soils. BSRs offer treatment conditions that are conducive to the optimal biotreatment of contaminated soils by slurrying contaminated soils in water using liquid-to-solid ratios ranging from 20 to 50 percent. The soil/water slurries are usually kept in suspension using mechanical mixers, injected air, recirculation pumps, and/or raker arms scraping the reactor bottom. Typically, BSRs are operated under aerobic conditions; however, BSRs can be configured for anaerobic treatment if warranted. BSRs can be operated in batch or continuous modes. Continuous flow systems are usually operated using multiple reactors in series. Figure 4-19 shows a typical schematic of a BSR system.

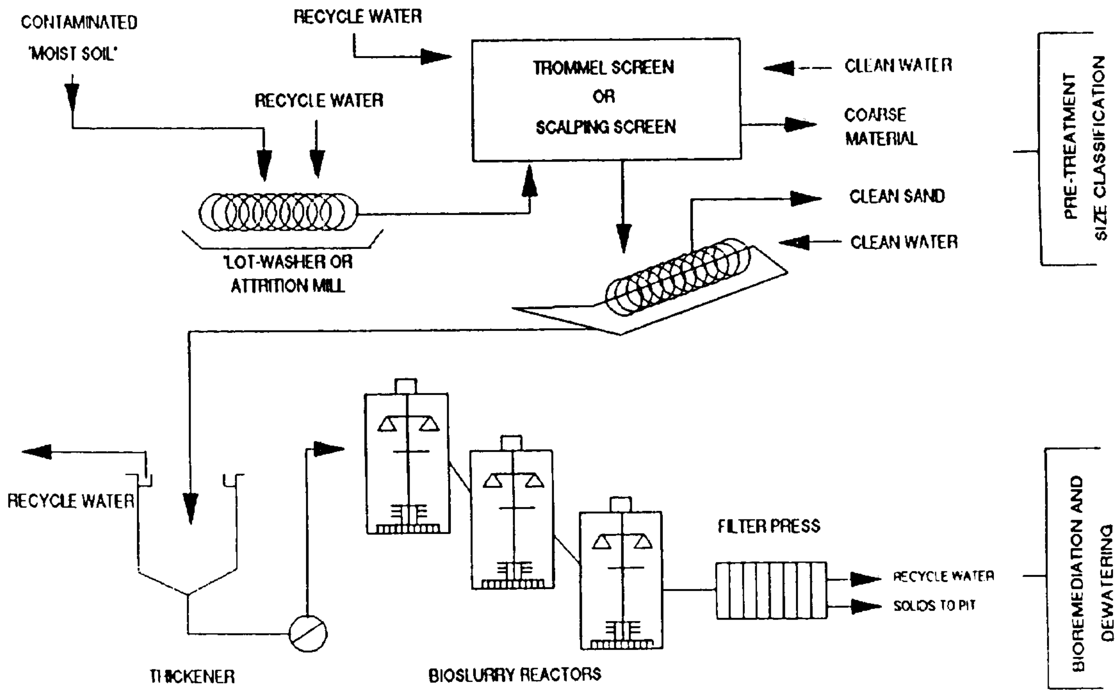


Figure 4-19. Typical Bioslurry Treatment System

(b) Many of the limiting conditions associated with other soil biotreatment technologies are substantially reduced in the BSRs. Oxygen transfer, usually a major limiting factor with the other soil treatment biotechnologies, especially in situ treatment, is improved due to increased mixing efficiency. Oxygen is supplied by the addition of air or oxygen via submerged gas spargers. Nutrients and co-metabolites may also be added depending on the required treatment conditions, usually determined through bench treatability studies. BSRs usually contain both attached and suspended growth consortia allowing for contaminant destruction in both phases. Microbial populations in BSRs are much higher than those found in other soil biotreatment systems due to the improved treatment conditions, thereby maximizing the degradation rate of contaminants due to improved microbe/contaminant contact and increased contaminant desorption rates.

(2) Applications.

(a) BSRs have proven effective in treating soils contaminated with petroleum hydrocarbon and wood preserving wastes. Some systems incorporate soil screening techniques prior to BSR treatment because the majority of the contaminants are sorbed to the finer fraction of the soils. BSR technology can be applied in custom fabricated, stock commercially available, or earthen reactor units. Soil residence times will vary greatly depending on the contaminant type, concentration, and sorption characteristics.

(b) Various additives can be provided to improve process performance. Surfactants have been proposed to increase the desorption rate of contaminants. Nutrient additive requirements, typically presented as the carbon: nitrogen:phosphate ratio (C:N:P), are usually on the order of 100:20:5; however, recent research indicates that increased ratios may increase contaminant degradation rates. Most contaminated soils contain native microorganisms capable of degrading the target contaminants that simply require stimulation by the addition of a limiting chemical species such as oxygen and/or nutrients. Treatment of sludges and soils which are devoid of native microbial populations may require the addition of a microbial inoculum.

(c) Residuals from BSRs are the soil/water slurry that may require separation (i.e., dewatering). The amount of dewatering required will be dictated by disposal plans for the treated soils. Aqueous solutions usually do not contain organic constituents due to the ease of degradation of the contaminants in solution.

(d) Potential waste streams from a BSR are off-gasing of volatile compounds and heavy-metals-contaminated soil/water slurries if the soil was also contaminated with heavy metals. Gas streams from a BSR can be either eliminated or reduced by use of pure oxygen or possibly an alternate electron acceptor. Gas streams can also be treated using activated carbon canisters.

(3) Advantages/disadvantages. The advantages and disadvantages of BSRs are summarized in below:

Advantages	Disadvantages
Rapid decontamination of contaminants.	Fairly energy intensive.
Numerous process variations which allow for high degree of flexibility.	Capital costs can be high.
Contaminated off-gasing can be easily controlled for complete elimination of contaminant release into the environment.	O&M intensive.
Higher contaminant concentrations compared to other soil biotreatment technologies can be treated due to higher microbial populations.	Requires soil excavation.
Process can be implemented in a variety of reactor systems.	May require soil dewatering.
	Few full-scale implementation verification data available.

(4) Data requirements. Principal data requirements for design of BSRs are determined through bench scale studies due to the lack of empirically based design formulas. The following factors should be evaluated in a properly planned bench study:

(a) Whether the target contaminants are best degraded under aerobic or anaerobic conditions.

(b) Benefits of co-metabolite addition.

(c) Benefits of surfactant addition.

(d) Optimum C:N:P ratios

(e) Potential for production of toxic chemical intermediates.

(f) Effect of addition of an exotic microbial inoculum.

(g) Retention time required to reach target contaminant levels.

(h) Optimum soil/water ratio.

(i) Potential for excessive foaming.

(5) Design criteria. Since there are few design criteria due to the limited evaluation and usage of this technology, the following design considerations must be addressed:

(a) Reactor volume - Reactor volume is dependent on soil retention time and required process flow.

(b) Soil screening - Required for soils containing either large coarse fractions or large debris that may damage the reactor.

(c) Mixing efficiency - High mixing efficiencies must be supplied to optimize the degradation rate of the target compound(s).

(d) Soil dewatering - May be required depending on soil disposal requirements.

(e) Oxygen requirements - Dependent upon the oxygen demands of the system determined during the bench study.

b. Composting.

(1) Composting is a biological treatment method which takes advantage of the heat of reaction during metabolism of organic carbon to sustain rapid decomposition. It is primarily used in treatment of sludges. There are three broad classifications of composting systems in use today. They are:

(a) Windrow system

(b) Aerated static piles

(c) In-vessel, mechanically agitated

(2) The windrow system is the simplest of the three and relies on natural aeration or periodic mixing as a means of supplying oxygen to the system and reducing excessive heat buildup. Specially designed windrow forming and turning machines have found application in large-scale operations.

(3) Aerated static piles provide an increased level of process control. Waste to be composted is typically placed in piles on top of channels or piping through which air may be blown or sucked through the piles. In simpler systems, a timer is used to periodically aerate the pile, the cycle of aeration is determined by trial. In more sophisticated systems, temperature feedback control is utilized to aerate the piles, maintaining a preset temperature. In most instances, temperature control through aeration provides greater than the required oxygen for metabolism.

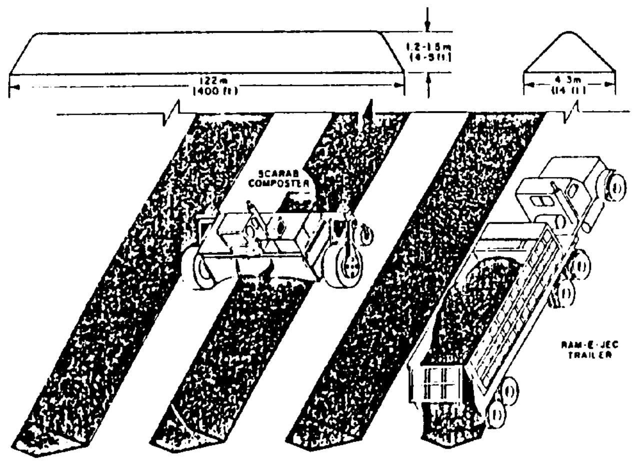
(4) The third system, the in-vessel, mechanically agitated system, is the most complex of the three and provides the highest degree of process control. Various designs have been developed. All allow composting in some form of vessel such as a tank, silo, or trench. Mechanical mixing of the compost through direct agitation or indirect tumbling is performed. Some systems incorporate forced aeration capabilities. As with aerated static piles, temperature is typically the control variable. In-vessel, mechanically agitated systems can be operated on a continuous basis. Figure 4-20 provides an example of the three types of systems.

(5) The primary objectives in sewage sludge treatment with composting are pathogen destruction, dewatering, and volume reduction. In some cases, the final product can be marketed as an agricultural additive. Essentially, the high temperatures achievable in compost systems are sufficient for pathogen destruction. Typically, 3 days at a temperature of 55 ^{0}C are required for pathogen destruction. Dewatering occurs as water in the compost mass is evaporated at the increased temperature. In aerated systems, water loss is even greater due to the transport out of the compost by the aeration stream. Volume reduction occurs as metabolism of the organic carbon with subsequent dewatering causes loss in mass and breakdown of internal structure. Addition of an amendment (additional organic carbon, nutrients, or inoculant) as well as bulking agents (wood chips, sawdust, hay, etc.) are often required to allow composting. In addition, water may be required as an additive during composting to maintain active conditions.

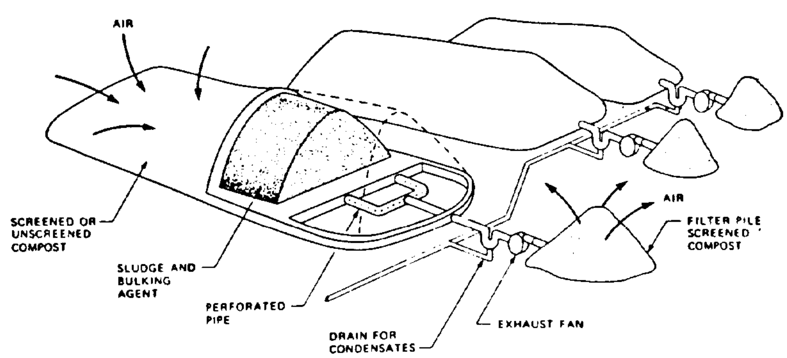
c. Applications.

(1) Composting is being used extensively in treatment of sewage sludge at municipal waste treatment plants. As optimum water content in the compost falls between 40 and 60 percent, composting usually does not involve a dewatering step prior to the process.

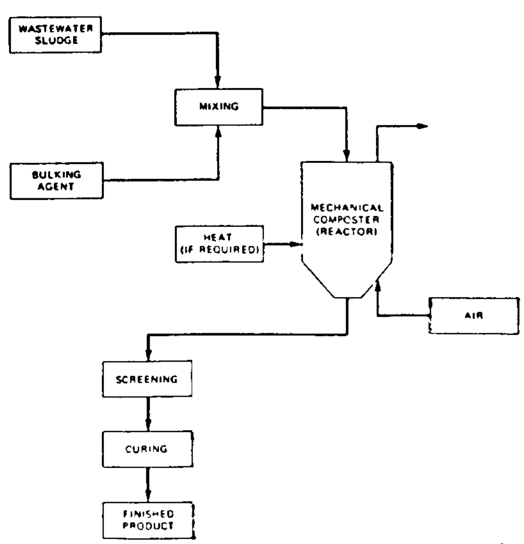
(2) Composting has been applied to a limited extent to process waste streams. Typically, it is more amenable to solid substrate treatment.



a. Typical windrow composting operation.



b. Typical aerated static pile composting system.



c. Typical in-vessel composting operation.

Figure 4-20. Typical Composting Systems

(3) Composting has recently been suggested for use in treatment of hazardous solid wastes. These include contaminated soils and sediments as well as hazardous solid waste from process industries.

d. Advantages/Disadvantages. The advantages/disadvantages of composting are summarized below:

Advantages	Disadvantages
No dewatering required	Treatment levels may be insufficient
Not energy intensive	Odors may present problems
Product may be agriculturally beneficial	Volume increase possible based on amendment requirements
Low capital investment for similar systems	Operation requires experienced personnel
Existing systems demonstrate reliability	

e. Data Requirements.

(1) Principal data requirements for the design of a compost system are very much dependent on the type of operation, either sewage sludge treatment, municipal/process waste treatment, or hazardous waste treatment. The difference comes in the objectives to be obtained. Some parameters required for all types include:

(a) Throughput (for sizing).

(b) Nitrogen and phosphorus levels (as nutrients).

(c) Bulk density (determines need for bulking).

(d) Water capacity (determines water requirements).

(e) Ambient temperatures (insulation).

(f) C:N ratio (amendment selection).

(2) For sewage sludge, the above should allow design estimates to be made as the compost must be maintained at 55 ^{0}C for 3 days. Dewatering and volume reduction of the compost mass can then be evaluated as required.

(3) For municipal/process waste treatment, something should be known about the kinetics of the thermophilic degradation of the particular waste stream. Half-life estimates or rate expressions are used to determine length of time required at the controlled temperature for completion.

(4) For hazardous waste treatment, kinetics of degradation must also be known for design. Contaminant availability in terms of desorption characteristics as well as solubility and vapor pressure become important parameters. If the hazardous waste is volatile at compost temperatures, means to control fugitive emissions must be incorporated.

f. Design Criteria.

(1) Key design parameters for composting include bulk density; carbon to nitrogen ratio (C:N ratio); water content; pile formation and shape; and mixing. Bulk densities of 1000 are considered optimum (this is for the composted material, bulking agent, and amendment mixture). Carbon to nitrogen ratios of 30 to 1 are considered optimum. Phosphorus levels are also important but are not felt to be as much an impact as nitrogen levels. A water content of between 40 and 60 percent may be necessary for good composting. The mixing of the compost matrix and subsequent formation into piles can play a large role in the effectiveness of composting. Bringing the ingredients into intimate contact within the solid matrix to allow microbial digestion requires good mixing. Pile design incorporates requirements for aeration and temperature distribution.

(2) Experience plays a large role in compost operations. Often, local recipes are used to construct the compost matrix based on experimentation on site. As composting is typically a longer term process, upsets can often be corrected before system performance degrades substantially.

(3) The pH of the compost material may play a role in operations, however; conflicting reports in the literature concerning the impact of changes in pH make prediction of the effect difficult. Within a range of 6 to 8 there appears to be no problem with pH. Outside this range site-wise determinations would likely have to be made.

(4) The finished compost may have value as an agricultural amendment. Levels of hazardous chemicals and elements play a key role in the final compost products disposal options or retail value.

(5) Selection of the type of system between windrows, static piles, and in-vessel mechanically agitated systems is dependent on many factors. The capital costs increase dramatically from the windrow to the mechanically agitated, in-vessel system. If levels of control are not necessary (including odor control and temperature) then a windrow system would be applicable. The capital cost of the mechanical system should be carefully weighed against the need for this level of process control. Insufficient data on increased reaction rates in these systems make selection difficult. If possible, pilot scale tests of the wastes to be composted should be conducted prior to selecting this form of composting system.

(6) Most compost systems do not require a large amount of specialized equipment. The backhoe and shovel appear as the most frequent equipment item necessary to conduct operations. Solids handling equipment to include conveyors are often used to increase throughput.

4-19. Encapsulation.

a. Process Description.

(1) Encapsulation is the process by which hazardous wastes are physically enclosed by a synthetic encasement to facilitate environmentally sound transport, storage, and disposal of the wastes. As a remedial action, encapsulation may be used to seal particularly toxic or corrosive hazardous wastes that have been removed from disposal sites. Encapsulation processes can be divided into two categories- -thermoplastic microencapsulation, and macroencapsulation (jacketing systems).

(2) Thermoplastic microencapsulation has been successfully employed in nuclear waste disposal and can be adapted to special hazardous wastes. The technique for isolating the waste involves drying and dispersing the material through a heated, plastic matrix. The mixture is then permitted to cool to form a rigid but deformable solid. In most cases it is necessary to use a container such as a fiber or metal drum to give the material a convenient shape for transport. The most common medium for waste incorporation is asphalt; but other materials such as polyethylene, polypropylene, wax, or elemental sulfur have been tried.

(3) Macroencapsulation systems contain potential pollutants by bonding an inert coating or jacket around a mass of cemented waste. This type of waste stabilization is unusual because the jacket or coating of the outside of the waste block is primarily responsible for isolating the waste from its surroundings.

b. Applications.

(1) Waste types that may require encapsulation include the following:

(a) Solid hazardous wastes in bulk or particulate form (e.g., severely contaminated sediments).

(b) Dewatered hazardous sludges.

(c) Containerized hazardous wastes (solids, sludge, or liquid) in damaged or corroded drums.

(d) Hazardous wastes which have been stabilized through solidification/cementation.

(2) TRW Systems Group has successfully developed bench-scale processes to agglomerate and encapsulate toxic and corrosive heavy metal sludges and soluble heavy metal salts, and to encapsulate containerized wastes. The agglomeration/encapsulation process involves mixing dried sludges (containing such hazardous heavy metals as arsenic, lead, mercury, selenium, beryllium, cadmium, zinc, and chromium) with a binder resin (modified 1,2-polybutadiene) and thermosetting the mixture in a special mold, while applying moderate mechanical pressure. The agglomerated material is a hard, tough, solid block. Encapsulating the waste/binder agglomerate with a 1/4-inch seamless jacket of

high density polyethylene (HDPE) is accomplished by packing powdered polyethylene around the block and then fusing the powder in situ with a second metal sleeve mold. A schematic diagram of the apparatus used to encapsulate the agglomerate is shown in Figure 4-21. A commercial-scale encapsulate produced by this method is expected to be a solid cube, 2 feet on edge, weighing 800 to 1,000 pounds. It would require approximately 8 percent (by weight) of polybutadiene resin for its fabrication. Additional jacket sizes will be available in the future.

(3) The second TRW macroencapsulation process is designed to enclose and seal waste containers such as 55-gallon drums (subject to corrosion rupture, leaks, and spills) using the same basic mold and fusion apparatus. To provide load-bearing ability, a 1/8-inch-thick interior casing of fiberglass is used to reinforce the 1/4-inch-thick HDPE jacket that encapsulates the container. A commercial-scale, fiberglass-reinforced HDPE encapsulate is envisioned to provide up to 284 ℓ (75 gallons) of capacity. The cylindrical jacket and casing would comprise about 5.3 percent (by volume) of the total encapsulate volume. Commercially, 7 mm (1/4-inch-thick) HDPE jackets can be fabricated in 30 seconds.

(4) Comprehensive laboratory testing of bench-scale encapsulates has demonstrated their ability to withstand severe mechanical stresses and biological and chemical degradation. Encapsulates containing wastes of various solubility were exposed to leaching solutions of various corrosivity; results indicate that the encapsulated wastes were completely isolated from, and resistant to, simulated disposal environment stresses. The encapsulates were also found extremely resistant to mechanical deformation and rupture. They exhibit high compressive strength and outstanding ability to withstand impact, puncture, and freeze-thaw stresses.

c. Advantages/Disadvantages. The major advantage of encapsulation processes is that the waste material is completely isolated from leaching solutions, and soluble hazardous materials such as heavy metal ions and toxic salts can be successfully encapsulated. The impervious HDPE jacket eliminates all leaching into contacting water (which may infiltrate or flow over disposal sites) and effectively contains hazardous waste substances that might otherwise migrate offsite. The advantages and disadvantages of encapsulation processes are as follows:

Advantages	Disadvantages
Cubic and cylindrical encapsulates allow for efficient space utilization during transport, storage, and disposal	Binding resins required for agglomeration/encapsulation (polybutadiene) are expensive
Hazard of accidental spills during transport is eliminated	Requires large expenditures of energy in fusing the binder and forming the jacket

(Continued)

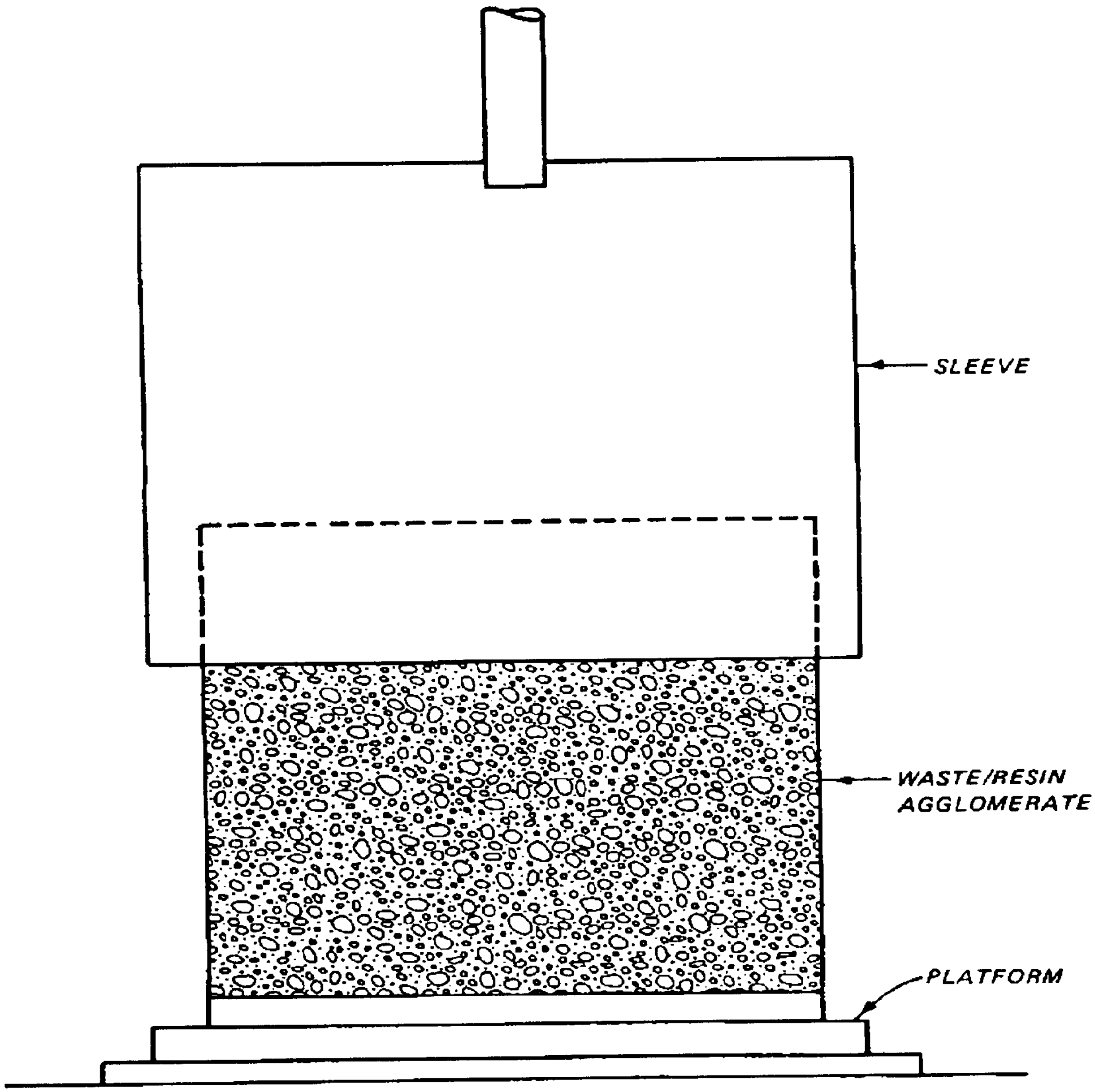


Figure 4-21. Encapsulation Process Concept
(Source: Lubowitz et al. 1977)

Advantages	Disadvantages
HDPE is low in cost, commercially available, very stable chemically, nonbiodegradable, mechanically tough, and flexible	Requires large capital investments in equipment
Encapsulated waste materials can withstand the mechanical and chemical stresses of a wide range of disposal schemes (e.g., landfill, ocean disposal)	Skilled labor is required to operate molding and fusing equipment
	Drying/dewatering of noncontainerized waste sludges is required for agglomeration/ encapsulation
	Process has yet to be applied on a commercial scale under actual field conditions

d. Data Requirements. Data requirements are similar to those required for solidification/stabilization described in paragraph 4-21.

e. Design Criteria.

(1) It is important to emphasize that encapsulation techniques have only recently advanced from the developmental and testing stages, and no large commercial-scale encapsulation facilities have been designed and operated as yet. It is likely that, as a remedial action, encapsulation will not be an economically feasible alternative compared to other direct waste treatment methods. However, a central solidification/encapsulating waste processing facility may be technically and economically feasible as a predisposal operation at hazardous waste storage and disposal facilities in the near future.

(2) The fabrication of commercial-scale encapsulates of containerized wastes under actual field conditions would require an encapsulation unit that is readily transportable to the storage or disposal site where containerized wastes reside. Where containerized wastes are of volumes smaller than the design capacity of the encapsulation unit, sand or soil may be used to fill voids between the container and encapsulate walls. Where very large volume waste containers require encapsulation (greater than 208 ℓ (55 gallons)), it may be necessary to install compaction operations at the site.

4-20. Low Temperature Thermal Desorption.

a. Process Description.

(1) Low temperature thermal treatment is a process of heating contaminated soil only enough to vaporize volatile organic compounds (VOCs). The gases emitted from the soil are then treated by a subsequent unit operation. The process described here as an example (Patent No. 4,738,206) uses indirect heat to separate the VOCs from the soil and incineration to destroy the VOCs in the gas phase. Maximum soil temperature for this process is 150 ^{0}C. The process was developed by the U.S. Army Environmental Center to treat soils at

military installations contaminated with trichloroethylene, dichloroethylene, tetrachloroethylene, xylene, and other components of solvents and petroleum fuels.

(2) The thermal processor for this system is a Holo-Flite screw conveyor heated by Dowtherm HT hot oil circulating through the shaft, blades, and jacket of the conveyor. A schematic diagram of the system is illustrated in Figure 4-22. Larger scale models may include two thermal processors operated in series with the first processor mounted on top of the second. Maximum temperature for the oil is 350 °C.

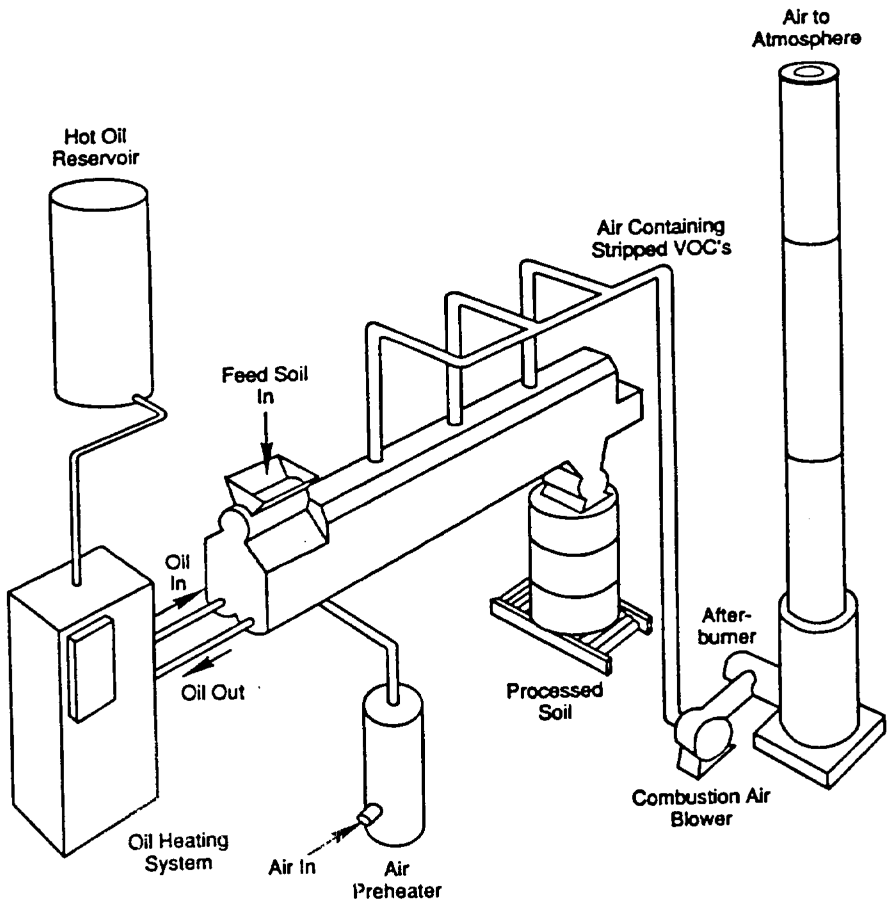


Figure 4-22. Schematic Diagram of a Low Temperature Thermal Treatment System

(3) The vapor stream from the thermal processor consists of the contaminants being removed, water vapor from the soil, and exhaust gases from the hot oil heater. This stream exits at approximately 150 °C (maximum) and flows through a fabric filter, condenser, afterburner, and caustic scrubber system. The fabric filter removes particulate carried over from the processor. The vapor stream then passes through an air-cooled condenser which reduces the temperature to approximately 52 °C. Water and organics condensed reduce the load on the afterburner. The afterburner is a gas-fired, vertical, fume incinerator operating at 980 °C. The afterburner is operated at a minimum of 3 percent excess oxygen. Exhaust from the afterburner is quenched

to approximately 80 ^{0}C. It then passes through a packed bed absorber where acid gases produced in the afterburner are neutralized with a caustic solution.

(4) A liquid stream is produced by the condenser which is water rich but does contain some hydrocarbons. The aqueous phase is separated from the organic phase in an oil-water separator. The aqueous phase is processed through a water treatment system consisting of fabric filters followed by granular activated carbon. This water is then used as makeup water for the scrubber and for dust control on processed soil. The organic phase from the separator may be either drummed for off-site disposal or injected into the afterburner.

(5) A system capable of processing 10 metric tons of soil per hour is mobile and can be transported to a site and assembled. Utilities required for operation are propane or natural gas, electricity, and process water. Discharges from the system include the scrubber stack exhaust, the processed soil, the granular activated carbon, and filter cake, and the organic phase from the water separator. Operation requires eight persons for continuous operation, including a site manager and an instrumentation technician.

b. Applications. Low temperature thermal treatment is capable of remediating soils contaminated with volatile and semivolatile compounds. Greater than 99 percent removal from soils has been demonstrated for trichloroethylene, dichloroethylene, and tetrachloroethylene, 1, 2-dichlorobenzene, l,3-dichlorobenzene, l,4-dichlorobenzene, toluene, naphthalene, and xylene. It has potential for application to a number of other volatile and semivolatile organic contaminants in soil.

c. Advantages and Disadvantages. Advantages of low temperature thermal treatment are summarized below:

Advantages	Disadvantages
Fully mobile system for on-site treatment	Limited applicability to higher boiling point organic compounds such as PCBs
Indirect heating provides greater thermal efficiency and reduced emission control requirements	Increased moisture content of soil increases costs
Afterburner destroys contaminants	Particle size reduction and debris removal may be required

d. Data Requirements. Design experience for application of this process to a wide range of soil types and contaminants is limited because of its recent development. Laboratory testing to determine optimum temperatures and retention times for the thermal processor should be conducted to develop the process design for the system. Important soil characteristics are grain size, moisture content, and contaminant concentrations.

4-21. Solidification/Stabilization.

a. Process Description.

(1) Solidification/stabilization technology as applied to wastes uses physical and chemical processes to produce chemically stable solids with improved contaminant containment and handling characteristics (Figure 4-23). Waste solidification is the term used to describe the process of sorbing a liquid or semiliquid waste onto a solid medium, such as fly ash, cement, kiln dust, or clay, or otherwise incorporating the waste in a solid matrix. This partial treatment eliminates any free liquid and reduces the risk of spillage or escape of contaminants in any liquid phase.

(2) Solidification may involve the addition of cementing agents so that the solid material (with the sorbed liquid) can be formed into a free-standing impermeable monolith. This part of the waste treatment process reduces the surface area across which transfer or loss of pollutants can occur. Stabilization of waste refers to chemical alteration of the waste so as to reduce the potential for escape of contaminants or to lower the toxicity of specific waste components. Both solidification and chemical stabilization result in transformation of liquid or semisolid wastes to an environmentally safer form. For example, metal-rich sludge would be considered solidified if it were mixed with a dry absorber such as fly ash or dry soil. The benefits of solidification could be carried further if the sorbent and waste were cemented into a permeable, monolithic block. The waste would be considered chemically stabilized if the chemical composition of the sludge were altered by the addition of lime ($Ca(OH)_2$) to raise the pH **so** that the potential contaminants (toxic metals) were less soluble and hence less easily leached. An absorbing medium can be formulated to take up free liquid and maintain conditions of lowered solubility for the potential contaminants. Cementing agents (organic polymers, pozzolanic materials, or portland cement) can be added to bind the stable, solid waste into a free-standing, relatively impermeable monolith that represents a substantially reduced environmental threat.

(3) Waste solidification/stabilization systems that have potentially useful application in remedial action activities discussed in this paragraph are: sorption, lime-fly ash pozzolan, and pozzolan-portland cement systems. Encapsulation processes such as thermoplastic microencapsulation and macroencapsulation were addressed in paragraph 4-19.

(a) Sorption. Most waste materials considered for solidification/stabilization are liquids or sludges (semisolids). In order to prevent the loss of drainable liquid and improve the handling characteristics of the waste, a dry, solid sorbent is generally added to the waste. The sorbent may interact chemically with waste or may simply be wetted by the liquid part of the waste (usually water) and retain the liquid as part of the capillary liquid. The most common sorbents used with waste include soil and waste products such as bottom ash, fly ash, or kiln dust from cement manufacture.

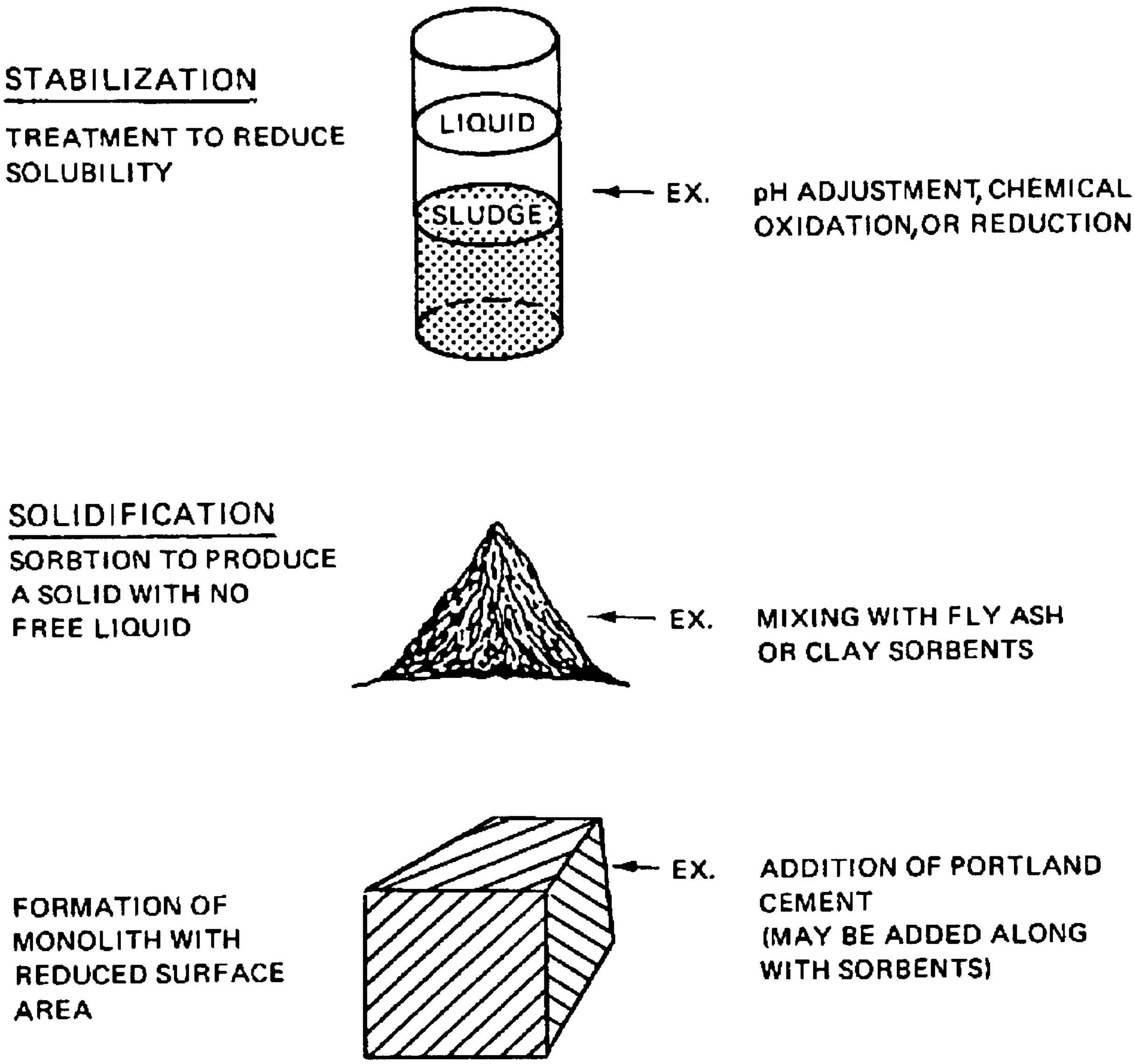


Figure 4-23. Steps in Stabilization/Solidification of Hazardous Wastes

In general, selection of sorbent materials involves tradeoffs between chemical effects, costs, and amounts required to produce a solid product suitable for burial. Table 4-18 summarizes chemical binding properties of natural sorbents for selected waste leach liquids. Where the ability of a sorbent to bind particular contaminants is important to containment, sorbents with specific chemical affinities can be selected. The pH of the waste strongly affects sorption/waste interactions, and pH control is an important part of any sorption process.

Table 4-18. Natural Sorbents and their Capacity for Removal of Specific Contaminants from Liquid Phases of Neutral, Basic, and Acidic Wastes

Contaminant	Neutral waste (calcium fluoride)		Basic waste (metal finishing sludge)		Acidic waste (petroleum sludge)	
Ca	Zeolite	(5054)*	Illite	(1280)	Zeolite	(1390)
	Kaolinite	(857)	Zeolite	(1240)	Illite	(721)
			Kaolinite	(733)	Kaolinite	(10.5)
Cu	Zeolite	(8.2)	Zeolite	(85)	Zeolite	(5.2)
	Kaolinite	(6.7)	Kaolinite	(24)	Acidic F.A.	(2.4)
	Acidic F.A.**	(2.1)	Acidic F.A.	(13)	Kaolinite	(0)
Mg	Basic F.A.	(155)	Zeolite	(1328)	Zeolite	(746)
			Illite	(1122)	Illite	(110)
			Basic F.A.	(176)	Basic F.A.	(1.7)
Zn					Zeolite	(10.8)
					Vermiculite	(4.5)
					Basic F.A.	(1.7)
Ni			Zeolite	(13.5)		
			Illite	(5.1)		
			Acidic F.A.	(3.8)		
F	Illite	(175)	Kaolinite	(2.6)	Illite	(9.3)
	Kaolinite	(132)	Illite	(2.2)	Acidic F.A.	(8.7)
	Acidic F.A.	(102)			Kaolinite	(3.5)
Total CN					Illite	(12.1)
					Vermiculite	(7.6)
					Acidic F.A.	(2.7)
COD	Acidic F.A.	(690)	Illite	(1744)	Vermiculite	(6654)
	Illite	(180)	Acidic F.A.	(1080)	Illite	(4807)
			Vermiculite	(244)	Acidic F.A.	(3818)

* Values represent sorbent capacity in micrograms of contaminant removed per gram of sorbent used.
** F. A. = fly ash. Acidic F.A. = Class F; Basic F.A. = Class C.

(b) Lime-fly ash pozzolan. Solidification/stabilization of waste using lime and pozzolanic material requires that the waste be mixed with a carefully selected, reactive fly ash (or other pozzolanic material) to a pasty consistency. Lime (calcium hydroxide) is blended into the waste-fly ash mixture. Typically 20 to 30 percent lime is needed to produce a strong pozzolan. The resulting moist material is packed or compressed into a mold to cure or is placed in the landfill and compacted.

(c) Pozzolan-portland cement. There are a wide variety of treatment processes that incorporate portland cement as a binding agent. Pozzolanic products (materials with fine-grained, noncrystalline, reactive silica) are frequently added to portland cement to react with any free calcium hydroxide and thus improve the strength and chemical resistance of the concrete-like product. In waste solidification, the pozzolanic materials (such as fly ash) are often used as sorbents. Much of the pozzolan in waste processing may be waste coated and relatively unreactive. Any reaction that does occur between the portland cement and free silica from the pozzolan adds to the product strength and durability. Waste solidifying formulations based on portland and pozzolan-portland systems vary widely, and a variety of materials have been added to change performance characteristics. These include soluble silicates, hydrated silica gels, and clays such as, bentonite, illite, or attapulgite. Approximate reagent requirements for some example applications are given in Table 4-19.

Table 4-19. Approximate Reagent Requirements for Various Waste Types Using a Portland Cement/Fly Ash Solidification[1]

Waste	Kilograms of reagent per liter of waste
Spent brine	3.8
Metal hydroxide sludge	2.4
Copper pickle liquor sludge	1.9
$FeCl_2$ pickle liquor sludge (1.5 percent HCl)	3.5
Sulfuric acid plating waste (15 percent (H_2SO_4)	3.8
Oily metal sludge	0.96

[1]After Stanczyk, Senefelder, and Clarke (1982). The proportion of portland cement to fly ash was not given.

b. Applications.

(1) Most large, hazardous waste landfills are currently employing sorption to satisfy requirements prohibiting burial of liquids. Nineteen million liters (five million gallons) of oil sludge from a former refinery site was landfilled onsite after treatment with cement kiln dust. The process required 3.71×10^7 kg (40,939 tons) of kiln dust.

(2) Lime-fly ash solidification/stabilization systems have been successfully used in managing hazardous waste, but generally the containment performance is such that a hazardous waste after processing would still be classed as hazardous. Lime-fly-ash-pozzolan-based landfills have been established using liner and monitoring systems to ensure safe disposal. There have been cases where lead wastes were judged nonhazardous after treatment, but in most cases a pozzolan-treated waste is not delisted.

(3) Pozzolan-portland-cement-based systems are among the most versatile. They can neutralize and seal acids and can handle strong oxidizers such as chlorates and nitrates. These methods are also good for solidifying many toxic metals, since at the pH of the cement (pH 9-11), many metals are insoluble carbonates and hydroxides.

c. Advantages/Disadvantages.

(1) Sorption has been widely used to eliminate free water and improve handling. Some sorbents have been employed to limit the escape of volatile organic compounds. Sorbents may also be useful in waste containment when they modify the chemical environment and maintain the pH and redox potential to limit the solubility of the waste. Although sorption eliminates the bulk flow of wastes from the site, in many cases leaching of waste constituents from the sorbent can be a significant source of pollution.

(2) The major advantages of the lime-fly ash solidification/stabilization technique include the ready availability and low cost of materials, and the familiarity of commonly used equipment. A disadvantage is that the solid mass resulting from lime-based solidification is porous. As such, it must either be sealed or placed in a secure landfill to prevent leaching of contained wastes. Another major disadvantage is that sludge or wastes containing organics cannot be treated.

(3) Provided pozzolan-portland cement based systems are used on compatible wastes, the short-term effectiveness can be expected to be quite good. The equipment for cement mixing is commonplace and the process is quite tolerant of chemical variations. However, because cement is a porous solid, contaminants can be leached out of the matrix over time and, therefore, these systems are usually not effective for organic wastes. Although it is possible to seal the outside of a block of cement-solidified wastes using styrene, vinyl, or asphalt to prevent leaching, no commercial systems are available to do this.

d. Data Requirements. The principal data requirements for solidification/stabilization techniques include:

(1) Waste characteristics (binding agent selection).

(a) pH.

(b) Buffer capacity.

(c) Water content.

(d) Total organic carbon.

(e) Inorganic and organic constituents.

(2) Treatability tests (cure time, mix).

(a) Leachability.

(b) Strength.

e. Design Criteria. The key design parameters for solidification/stabilization techniques include:

(1) Solidification mixing ratios.

(2) Curing time.

(3) Volume increase of solidified product.

f. Evaluation. The evaluation of these factors is dependent on the solidification technology and the specific waste being treated.

4-22. Thermal Destruction.

a. Process Description. Incineration combusts or oxidizes organic material at very high temperatures. The end products of complete incineration are CO_2, H_2O, SO_2, NO_1, and HCl gases. Emission control equipment (scrubbers, electrostatic precipitators) for particulates, SO^2, NO_x, and products of incomplete oxidation are needed to control emissions of regulated air pollutants. Common types of incinerators most applicable to hazardous waste include:

(1) Rotary kilns.

(2) Multiple hearth.

(3) Fluidized bed.

(4) Liquid injection.

The key features of incineration methods cited previously are summarized in Table 4-20.

Table 4-20. Key Features of Major Types of Incinerators

Type	Process principle	Application	Combustion temp.	Residence time
Rotary kiln	Slowly rotating cylinder mounted at slight incline to horizontal. Tumbling action improves efficiency of combustion	Most organic wastes; well suited for solids and sludges; liquids and gases	810-1,640 °C (1,500-3,000 °F)	Several seconds to several hours
Multiple hearth	Solid feed slowly moves through vertically stacked hearths; gases and liquids feed through side ports and nozzles	Most organic wastes, largely in sewage sludge; well suited for solids and sludges; also handles liquids and gases	760-980 °C (1,400-1,800 °F)	Up to several hours
Liquid injection	Vertical or horizontal vessels; wastes atomized through nozzles to increase rate of vaporization	Limited to pumpable liquids and slurries (750 SSU Saybolt Seconds Universal) or less for proper atomization)	650-1,650 °C (1,200-3,000 °F)	0.1 to 1 sec
Fluidized bed	Wastes are injected into a hot agitated bed of inert granular particles; heat is transferred between the bed material and the water during combustion	Most organic wastes; ideal for liquids, also handles solids and gases	750-870 °C (1,400-1,600 °F)	Seconds for gases and liquids; longer for solids

b. Applications.

(1) Incineration is used for reduction of sludge volume, thereby reducing land requirements for disposal. Incineration can also be used to destroy most organic wastes whether they be gas, liquid, or solid.

(2) Mobile incineration systems have been considered for onsite treatment at hazardous waste sites. The EPA*s Office of Research and Development has completed construction and is in the testing phase of a mobile incineration system. The system was designed to EPA*s PCB destruction specifications to provide state-of-the-art thermal detoxification of long-lived, refractory organic compounds, as well as debris from cleanup operations. Hazardous substances that could be incinerated include compounds containing chlorine and phosphorous--for example, PCB*s, kepone, dioxins, and organophosphate pesticides, which may be in pure form, in sludges, or in soils. A typical mobile incinerator is illustrated in Figure 4-24.

c. Advantages/Disadvantages. The advantages and disadvantages of hazardous waste treatment with incineration are summarized below:

Advantages	Disadvantages
Can destroy a wide range of organic wastes	Thickening and dewatering pretreatment may be required
Can handle gaseous, liquid, and solid wastes	May not be economical for small plants
	Air pollution control measures are required

d. Data Requirements. The principal data requirements for the design of an incineration system are:

(1) Waste constituents and characteristics.

(a) Moisture content.

(b) Volatile materials content.

(c) Ash content.

(d) Ash specific level, specific gravity, or bulk density.

(e) Ash particle size range.

(f) Carbon, hydrogen, oxygen, halide, sulfur, nitrogen, phosphorus content.

(g) Waste specific gravity, viscosity, and melting point.

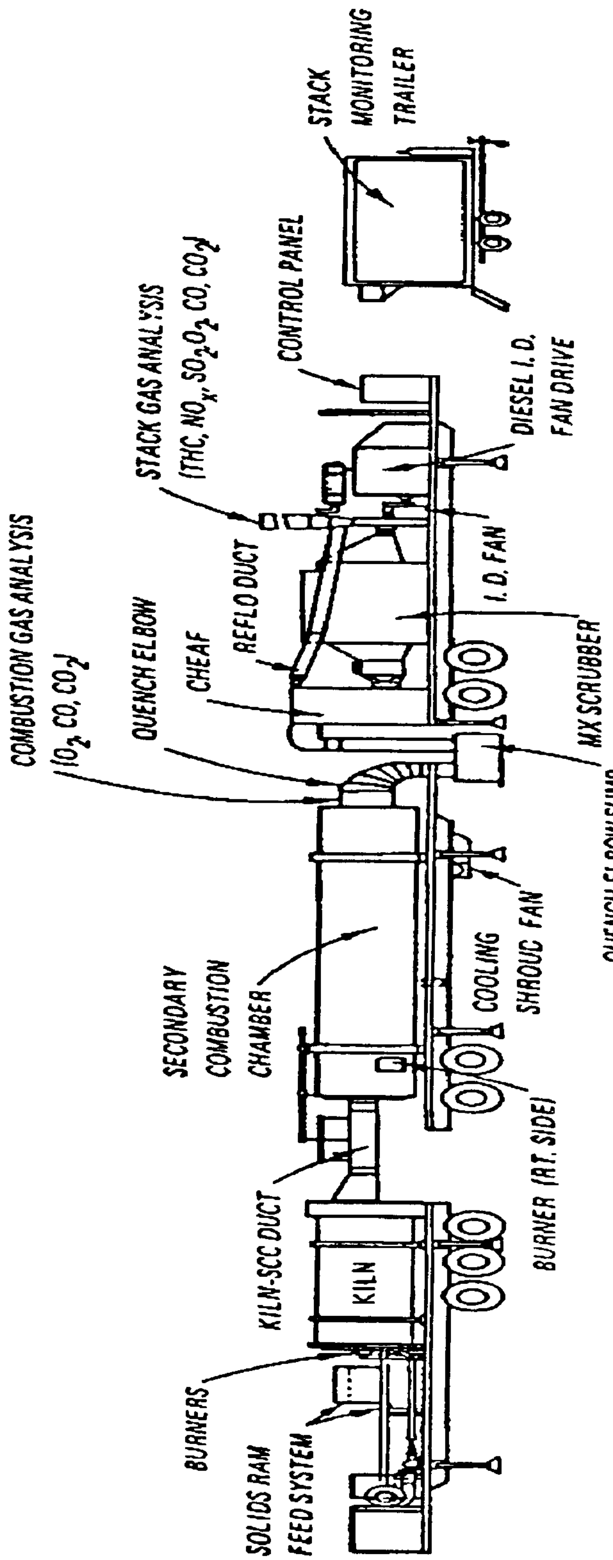


Figure 4-24. EPA Mobile Incineration System

(h) Metal content.

(i) Thermogravimetric analysis.

(j) Suspended and dissolved solids.

(k) Reactive chemical groups.

(l) Flammability, stability, detonation.

(m) Environmental sensitivity.

(n) Toxicity.

(2) Process characterization.

(a) Residence time.

(b) Temperature.

(c) Destruction efficiencies.

(d) Ash residue.

(e) Gaseous effluent.

e. Design Criteria. The design criteria for a fluidized bed furnace (FBF) and a multiple hearth furnace (MHF) are presented in Tables 4-21 and 4-22, respectively. During actual operations some extensive maintenance problems have occurred with air preheaters. Venture scrubbers have also had scaling problems. Screw feeds and screw pump feeds are both subject to jamming because of either overdrying of the sludge feed at the incinerator or because of silt carried into the feed system with the sludge. Fluidized bed furnace systems have had problems with the burnout of spray nozzles or thermocouples in the bed.

Table 4-21. Design Criteria for Fluidized Bed Furnace

Parameter	Design criteria
Bed loading rate	245 to 294 kg/m^2/hr (50 to 60 lb wet solids/ ft^2/hr)
Superficial bed velocity	0.12 to 0.18 m/s (0.4 to 0.6 ft/sec)
Sand effective size	0.2 to 0.3 mm (uniformity coefficient = 1.8)
Operating temperature	760 to 816 °C (1,400 to 1,500 °F) (normal); 1204 °C (2,200 °F (maximum))
Bed expansion	80 to 100 percent
Sand loss	5 percent of bed volume per 300 hr of operation

Table 4-22. Design Criteria for Multiple Hearth Furnace

Parameter	Design criteria
Maximum operating temperature	927 °C (1,700 °F)
Hearth loading rate	29.4 to 49 kg/m²/hr ((6 to 10 lb wet solids/ft²/hr) with a dry solids concentration of 20-40 percent
Combustion airflow	12 to 13 kg/kg dry (12 to 13 lb/lb dry solids
Shaft cooling airflow	1/3 to ½ of combustion airflow
Excess air	75 to 100 percent

4-23. Volume Reduction.

a. Process Description.

(1) Volume reduction as applied to sludges can be termed as thickening or dewatering processes. Thickening of sludge consists of the removal of supernatant, thereby reducing the volume of sludge that will require disposal or treatment. Gravity thickening takes advantage of the difference in specific gravity between the solids and water.

(2) Centrifuges are used to dewater sludges using centrifugal force to increase the sedimentation rate of sludge solids. During the process of centrifugation, if a particle is more dense than the fluid, it will tend to migrate in the direction of the centrifugal force, i.e., toward the periphery of the rotating vessel containing the fluid. If the particle is less dense than the fluid, there will be a tendency for the particle to remain near the center of rotation and the fluid to migrate toward the periphery of the vessel. Either way, particles that were uniformly dispersed throughout the fluid prior to centrifugation would now be concentrated in a specific region of the centrifuge where they can be removed as a more concentrated mixture. In centrifugation, the centrifugal force is analogous to gravitational force in the sedimentation process. In centrifugation, however, forces equal to several thousand times the force of gravity are often generated.

(3) Volume reduction will frequently be required to meet regulatory restraints as applied to disposal of hazardous waste. Disposal costs can be reduced through the use of volume reduction techniques by eliminating nonhazardous free liquids from a waste. Before a hazardous waste can be disposed of at a chemical waste landfill, it must be solidified. Typically the solidification process will add to the total weight and volume and therefore the disposal costs. If the same waste can be separated into a reduced volume of hazardous solid waste and a nonhazardous liquid waste, disposal costs can be lowered significantly.

b. Applications. Dewatering and thickening processes have been used primarily to thicken primary, secondary, and digested sludges. Centrifuges may be used for thickening sludges where space limitations or sludge characteristics make other methods unsuitable. However, if a particular sludge can be effectively thickened by gravity without chemicals, centrifuge thickening is not economically feasible. Centrifuges are generally used for dewatering sludge in larger applications where sludge incineration is required.

c. Advantages/Disadvantages. Gravity thickening is highly dependent on the dewaterability of the sludges being treated while centrifugal thickening processes can have significant maintenance and power costs. Adequate electric power must also be provided for the large motors that are required. Depending on the waste, the liquid fraction after centrifugation may be considered hazardous also and require proper disposal. Typically the liquid fraction will be relatively high in suspended nonsettling solids.

d. Data Requirements. The data requirements for gravity thickening or centrifugation include:

(1) The waste stream daily flow.

(2) Settling velocity.

(3) Size distribution.

(4) Solids specific gravity.

(5) Liquid specific gravity.

e. Design Criteria.

(1) For gravity thickeners detention times of 1 to 3 days are used, sludge blankets of at least 3 feet are common, side water depths of at least 10 feet are a general practice, and surface loading rates can range from 5 to 25 pounds per day per square foot depending on the sludge type and pretreatment used.

(2) Each installation of a centrifuge is site specific and dependent upon a manufacturer*s product line. Maximum capacities of about 9.1×10^4 kg (100 tons per hour) of dry solids are available in solid-bowl units with diameters up to 1.4 m (54 inches) and power requirements up to 130 KW (175 horsepower). Disk-type units are available with capacities up to 1.5 m^3/min (400 gallons per minute) of concentrate.

4-24. Wet Oxidation.

a. Process Description.

(1) Wet air oxidation (WAO) is truly an oxidation process. Thermodynamically, it is similar to chemical oxidation and incineration.

(2) The waste is pumped into the system by the high-pressure pump and mixed with air from the air compressor. The mixture passes through a heat exchanger and then into the reactor where oxygen in the air reacts with organic matter in the waste. This oxidation is accompanied by a temperature rise. The gas and liquid phases are separated after the reactor, and the liquid passes through the heat exchanger heating the incoming material. The gas and liquid streams are discharged from the system through control valves.

(3) As would be expected, the operating temperature is critical. Organic molecules are excited thermally (as opposed to UV light) to a level where a high percentage undergo an oxidization reaction. As expected, various materials require different energy levels for a significant reaction rate to take place. Figure 4-25 shows the relationship between temperature and degree of oxidation for several different materials. At 150 °C, 5 to 10 percent of the COD may be oxidized, whereas at 320 °C, nearly complete oxidation occurs for many substances.

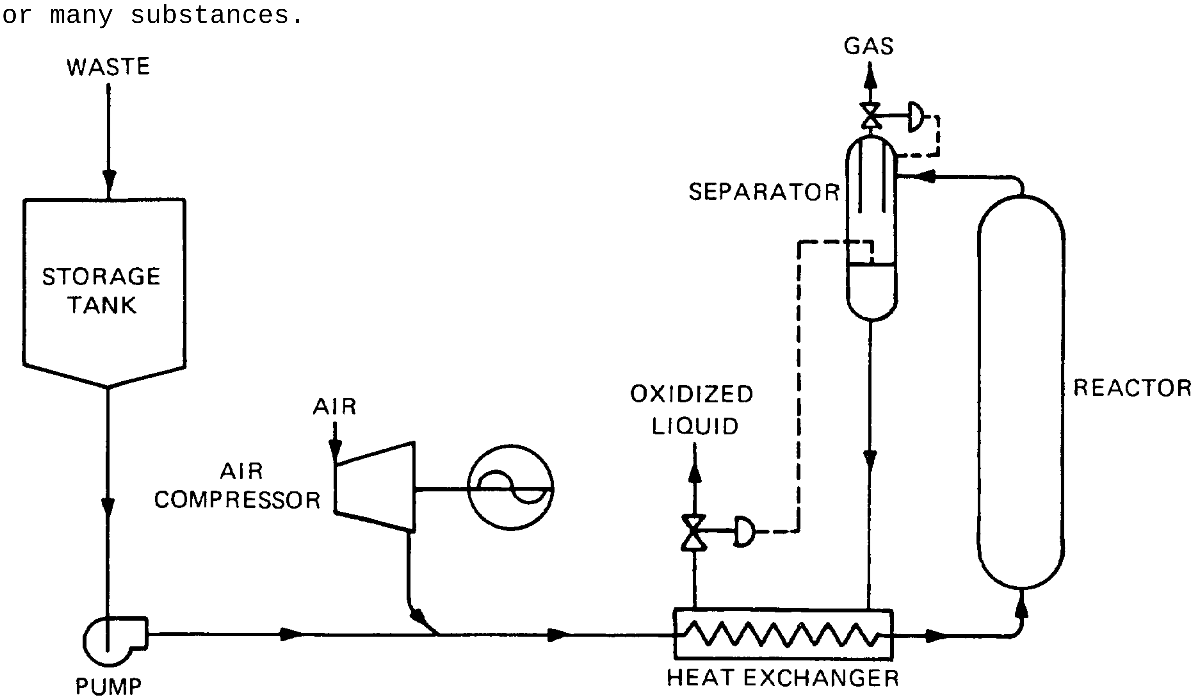


Figure 4-25. Flow Sheet of Wet Air Oxidation

b. Applications.

(1) WAO conditions can be controlled to achieve a desired end product by controlling the temperature and the reaction time. With increased temperature, the degree of oxidation increases as shown in Figure 4-26. As the oxidation condition becomes more severe, more of the nonbiodegradable components of the waste are converted to biodegradable forms. WAO may be used as a treatment to detoxify a waste before biological treatment. This technique has been used to treat acrylonitrile wastewaters that are highly concentrated in cyanide and organic nitrites.

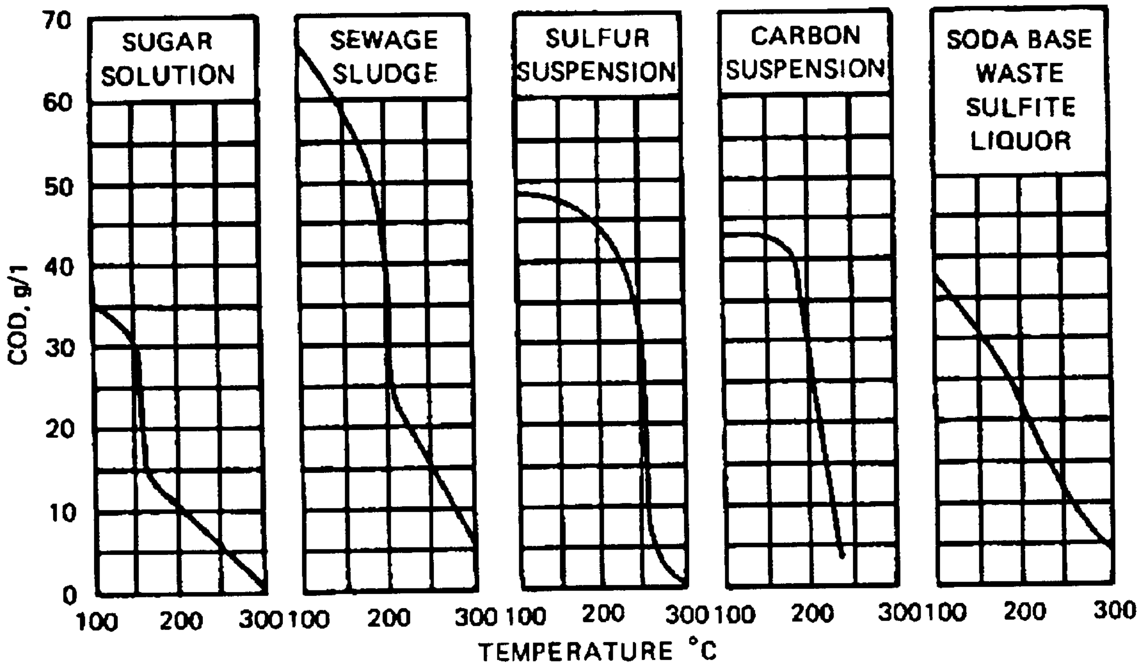


Figure 4-26. Oxidation Curves for Five Aqueous Fuels

(2) WAO may be well suited for treating hazardous waste. Recent studies have focused upon some of the 65 priority pollutants originally proposed by the EPA. Results are shown in Table 4-23. It should be observed that operating conditions were fairly stringent (275 to 320 °C and 6200 to 12,400 KPa (900 to 1800 pounds per square inch) atmosphere (psia)). However, removal percentages are impressive. It is not clear if these reductions represent a conversion to CO_2 or simply a modification to the original molecule. It should be noted that most of the materials in Table 4-23 are aromatic derivatives. In many cases, the toxicity of aromatics is greatly reduced by simply opening the ring structure of the molecules. This would require only fractional oxidation.

c. Advantages/Disadvantages.

(1) WAO is an exciting oxidative process that appears to have wide application along with versatility and flexibility. Almost any combustible materials, organic or inorganic, can be treated by WAO. The question of economics affects selection of this process since it is energy intensive.

(2) Typically WAO should be considered as a step in the overall waste treatment process. It is rarely used as the total treatment. WAO may not be reasonable for waste containing less than 2,000 milligrams per liter COD. Depending upon capital and the nature and treatability of the waste, it may be desirable to treat by another method or to concentrate to reduce the volume prior to WAO treatment.

Table 4-23. Examples of One-Hour Oxidation of Selected Compounds

Compound	Starting Concentration (g/ℓ)	% Starting material destroyed 320°C	275°C	275°C/* Cu^{++}
Acenaphthene	7.0	99.96	99.99	-
Acrolein	8.41	99.96	99.05	-
Acrylonitrile	8.06	99.91	99.00	99.50
2-Chlorophenol	12.41	99.86	94.96	99.88
2,4-Dimethylphenol	8.22	99.99	99.99	-
2,4-Dinitrotoluene	10.0	99.88	99.74	-
l,2-Diphenylhydrazine	5.0	99.98	99.98	-
4-Nitrophenol	10.00	99.96	99.60	-
Pentachlorophenol	5.0	99.88	81.96	97.30
Phenol	10.0	99.97	99.77	-

* Cupric sulfate was added as a catalyst.

(3) Primary other advantages and disadvantages are summarized below:

Advantages	Disadvantages
May be controlled to deliver a specific degree of oxidation	Requires operation at high pressure and temperatures
Can be used to detoxify toxic materials	Corrosive inorganics can be a problem at high temperatures
No net heating requirement if the COD is >15,000 mg/ℓ	Initial capital costs are high
	Primarily suited for pretreatment as reductions of 10 to 15% are typical

d. Data Requirements. In general, bench scale and/or pilot scale testing will be required for design. The following parameters should be determined:

(1) COD of wastes.

(2) TDS of wastes.

(3) Operating temperature.

(4) Retention time.

(5) Degree of stabilization.

(6) Degree of detoxification.

e. Design Criteria.

(1) Due to the critical nature of the temperature, the operating system becomes a prime design parameter. Not only will the system require specific design for a specified operating pressure but also the compressor system must be capable of delivering air or oxygen at the maximum operating pressure expected in the system. Table 4-24 presents data on the temperature-pressure relationship of steam.

Table 4-24. Temperature/Pressure Relationship of Saturated Steam

Pressure (psia)	Pressure (KPa)	Temperature (°C)	Temperature °(F)
100	689	212	14.7
125	861	257	34
150	1034	302	69
175	1206	347	130
200	1378	392	226
225	1550	437	371
250	1722	482	577
275	1895	527	863
300	2067	572	1248
325	2239	617	1762

(2) As a general rule, the maximum operating temperature will be about 200 °C. Higher temperatures may be reached but at the expense of a large increase in pressure.

(3) If the COD of the waste is less than 15,000 milligrams per liter, consideration should be given to concentrating the waste stream prior to WAO treatment.

4-25. Evaporation.

a. Background.

(1) Evaporation is a technique used for many years in the process industry. It is also used in waste treatment applications. In concept, evaporation is no more complicated than placing a pot on a stove and evaporating the contents. It is not a necessary criterion to carry to dryness.

(2) The objective of evaporation is to reduce the volume of waste to handle by concentrating a solution consisting of a nonvolatile solute and a volatile solvent, In the overwhelming majority of evaporations applicable to

toxic waste sites, the solvent is water. Evaporation is conducted by vaporizing a portion of the solvent to produce a concentrated solution or a thick liquor.

(3) Evaporation differs from drying in that the residue is often a highly viscous liquid, rather than a solid; it differs from distillation in that the vapor is usually a single component, and even when the vapor is a mixture, no attempt is made in the evaporation step to separate the vapor into fractions; it differs from crystallization in that the emphasis is placed on concentrating a solution rather than forming and building crystals. In certain situations, however (for example, in the evaporation of brine to produce salt), the line between evaporation and crystallization is not distinct. Evaporation sometimes produces a slurry of crystals in a saturated mother liquor.

(4) It appears that evaporation will remain a popular unit operation for many years to come even though energy requirements are very significant. As manufacturing facilities push toward zero discharge through various recycling and recovery programs, evaporation will play an important role in closing the loop in many of these operations.

b. Process Description.

(1) There are many types of evaporators currently in use in the industrial scene. The intent here is to introduce only the most likely processes which may be applicable to hazardous waste problems. Evaporator systems may be single or multiple effect. This is analogous to saying they may be single or multiple stages.

(2) Single-effect evaporators are used where the required capacity is small, steam is cheap, the vapors or the liquids are so corrosive that very expensive materials of construction are required, or when the vapor is so contaminated that it cannot be used for steam. Single-effect evaporators may be operated in batch, semibatch, continuous batch, or continuous mode. In any configuration, the single-effect system is the most energy intensive with the least capital expenditure.

(3) Perhaps the most widely used configuration is the multiple-effect scheme. The choice of the number is up to the designer. Most textbooks and references to multiple-effect evaporators will typically show three effects as shown in Figure 4-27. However, a system may theoretically have an infinite number of effects. On the practical side, the number of effects will be limited by a balance between capital cost and operating cost. Vapor from the first effect is used as steam for the second effect and so on. Steam economy of a multiple-effect evaporator will increase in proportion to the number of effects, but will be somewhat less numerically than the number of effects. A system designed for producing pure water from seawater uses a 20-effect system. The steam-to-product ratio is 1 to 19. The increased steam economy is offset by an increase in capital expenditure.

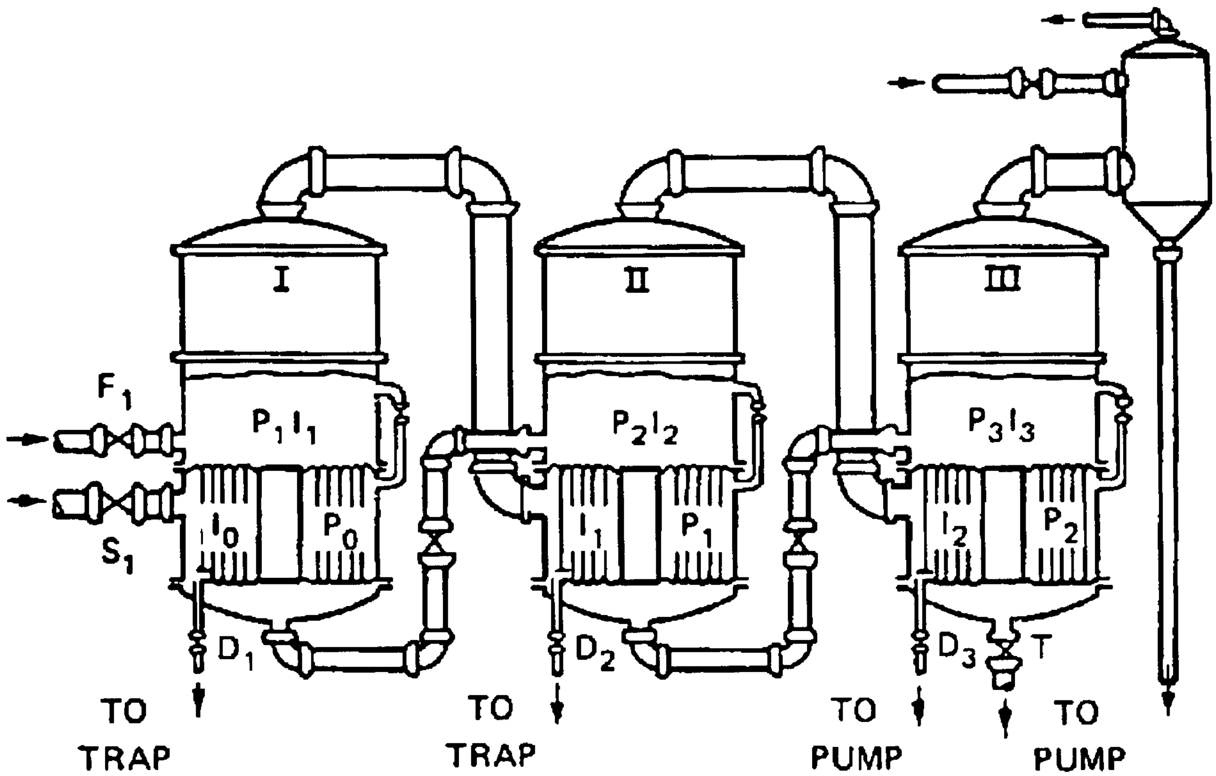


Figure 4-27. Three-Effect Evaporator.

(4) Energy requirements for evaporation will vary widely depending on the number of effects used as indicated above. Also, the heat transfer coefficients for a particular system will influence the energy requirements. The normal operating range of energy for evaporation is 6.45×10^{-2} to 0.71 KW/hr/Kg H_2O (100 to 1,100 BTU*s per pound of water) evaporated. The latter value assumes a single-effect system with little heat recovery.

c. <u>Applications</u>. Evaporation is a well-defined, well-established process that is essentially omnipresent in industry. It is being used currently for the treatment of hazardous waste such as radioactive liquids and sludges, concentrating of plating and paint solvent waste, and in the pulp and paper industry, six-effect evaporators are typically used to concentrate black liquor while producing methanol. It is capable of handling liquids, slurries, and sometimes sludges, both organic and inorganic, containing suspended or dissolved solids or dissolved liquids where one of the components is essentially nonvolatile. It can be used to reduce waste volume prior to incineration or precipitation.

d. <u>Advantages/Disadvantages</u>. A summary of advantages and disadvantages is presented below:

Advantages	Disadvantages
Not a new technology; has been used many years in the chemical process industries	Energy intensive process, offset somewhat by multiple-effect operation
Large volume reductions can be realized	Evaporation tubes are easily fouled, lowering heat transfer coefficients
Effective pretreatment step prior to incineration	Requires a source of steam
Condensate may be marketable	Bottoms and condensate may require further treatment or disposal

e. Data Requirements. Data requirements include:

(1) Thermodynamic data for stream being evaporated, i.e., sensible heat, heat of vaporization over concentration range, heat of crystallization.

(2) Feed flow rate and temperature.

(3) Pressure and/or temperature of available stream.

(4) Vacuum or boiling temperature of the last stage.

(5) Suitability of vapor from first stage as steam for the second stage, etc.

(6) Quality of water to be evaporated, i.e. extent of concentration.

(7) Number of effects or stages to be used.

(8) Heat transfer coefficients as a function of boiling temperature and)t.

f. Design Criteria.

(1) Evaporation systems are generally designed to balance the cost between capital and operating costs. As additional effects are added to a system, the more energy efficient the system becomes. This savings in energy will be at the expense of capital cost. At some point, an optimum number of effects will be realized. The number of effects is also constrained by the available steam pressure for the first stage and the vacuum for the last stage. Still another consideration is the quantity of material to be processed. For very small volumes, a single stage may be sufficient.

(2) For waste treatment applications, the number of effects may be established on the basis of the available quantity and quality of steam along with good engineering judgment. Heating surfaces in all effects of a multiple effect system should be equal to obtain economy of construction. Design procedures are presented in Badger and Banchero (1955) and DeRenzo (1978). Metry (1980) should be consulted for heat transfer considerations.

Section III. In Situ Treatment Technologies

4-26. Biological Treatment.

a. Process Description.

(1) Organic materials in contaminated soils may be amenable to biodegradation in place, or in situ. The process consists largely of producing conditions in the soil mass which promote the rate of natural degradation by endogenous organisms. Conditions favoring biodegradation include increased aeration and nutrient concentrations. In some cases, seed cultures may increase the active population and be beneficial.

(2) The biodegradation process is slow relative to other remedial action technologies. Complete degradation of the waste could take several years and may never be complete if refractory compounds such as polynuclear aromatics are present. This is a major disadvantage, since additional migration of contaminants can occur during the treatment and even afterwards.

(3) This technique is generally limited to those situations where the waste material or contaminated soil is naturally aerated or where artificial aeration is feasible. Procedures for the addition of nutrients such as nitrogen and phosphorus may be necessary if the waste material is deficient in these constituents. Lime may be required to maintain proper pH.

b. Applications.

(1) Situations where in situ bioremediation could be applied are those where complete mixing and/or aeration can be achieved. A primary application is a chemical spill or landspreading operation where the wastes have not migrated below tilling depth (about 305 to 610 mm (12 to 24 inches)), or a surface impoundment in which the waste is fluid enough to be mechanically aerated and pumped for mixing.

(2) Biodegradation has been used most widely for treatment of oily sludges and refinery waste. Chlorinated solvents such as TCE or PCE are not degraded effectively using current technology; however, work is continuing on these materials. Naturally occurring bacteria and special cultures have been developed which are capable of degrading benzene, phenol, cresol, naphthalene, gasoline, kerosene, and cyanide, and many of their derivities.

c. Advantages/Disadvantages. In land treatment, if soils are not well aerated, waste degradation will occur only slowly, if at all. Because metals are not degraded, careful attention should be given to the toxic metal load at the site. Since the process can be very slow, additional migration of contaminants may take place during and after treatment. Also, the possibility of forming a toxic byproduct as a result of biodegradation should be considered.

d. Data Requirements.

(1) The type, quantity, and distribution of the waste constituents will have to be determined to select a nutrient, and air requirements.

(2) Tests must be made to determine if microorganisms are naturally occurring which will breakdown the target chemicals. If none are present, enriching or seed cultures may be required.

(3) The site topography, hydrogeology, and soil physical, chemical, and biological properties are also necessary to determine the injection and withdrawal system requirements and design.

e. Design Criteria. The key factors for biodegradation include:

(1) Nutrient balance.

(2) pH maintenance.

(3) Soil aeration and/or oxygen availability.

(4) Degradation rate of waste constituents.

(5) Waste constituents and location.

4-27. Chemical Oxidation.

a. Process Description. In-situ leachate treatment introduces a reactant into the contaminated region to interact with the leachate plume. Chemical injection entails injecting chemicals into the ground beneath the waste (see Figure 4-28) to neutralize, precipitate, or destroy the leachate constituents of concern.

b. Applications. Sodium hypochlorite has been used to treat leachate containing cyanide (Tolman et al. 1978). Very little field data are available. The areal spread and depth of the leachate plume must be well characterized so that injection wells can be placed properly to intercept all of the contaminated ground water.

c. Advantages/Disadvantages.

(1) Pollutants may be displaced to adjacent areas when chemical solution is added.

(2) Hazardous compounds may be produced by reaction of injected chemical solution with waste constituents other than the treatment target.

d. Data Requirements. The principal data requirements include the contamination plume characteristics: depth to bedrock, plume cross section, leachate or ground-water velocity, and hydraulic gradient. Also the soil permeability, leachate composition, and reaction rates will have to be determined.

e. Design Criteria. Chemical injection systems are in the conceptual stage of development. The permeability of the soil beneath the waste must be known to determine the ground-water flow through the injected waste and the reaction time between the contaminated ground-water and chemicals.

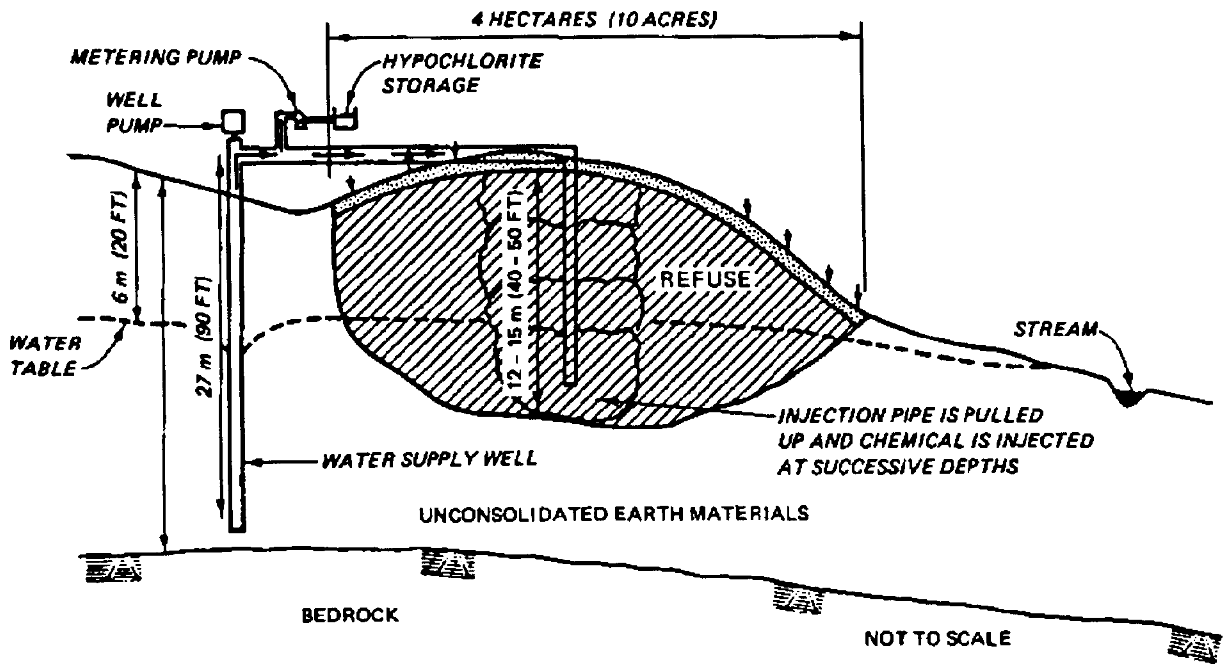


Figure 4-28. Cross Section of Landfill Treated by Chemical Injection

4-28. Permeable Treatment Beds.

a. Process Description. Permeable treatment beds use trenches filled with a reactive permeable medium to act as an underground reactor (see Figure 4-29). Contaminated ground water or leachate entering the bed reacts to produce a nonhazardous soluble product or a solid precipitate.

b. Applications.

(1) Permeable treatment beds are applicable in relatively shallow aquifers since a trench must be constructed down to the level of the bedrock or an impermeable clay. Permeable treatment beds often are effective only for a short time as they may lose reactive capacity or become plugged with solids. Overdesign of the system or replacement of the permeable medium can lengthen the time period over which permeable treatment is effective.

(2) The materials used for this form of treatment are:

(a) Limestone or crushed shell- -Limestone neutralizes acidic ground water and may remove heavy metals such as Cd, Fe, and Cr. Dolomitic limestone ($MgCO_3$) is less effective at removing heavy metals than calcium carbonate limestone. The particle size of the limestone should match a mix of gravel size and sand size. The larger sizes minimize settling of the bed and channeling as the limestone dissolves. The small sizes maximize contact.

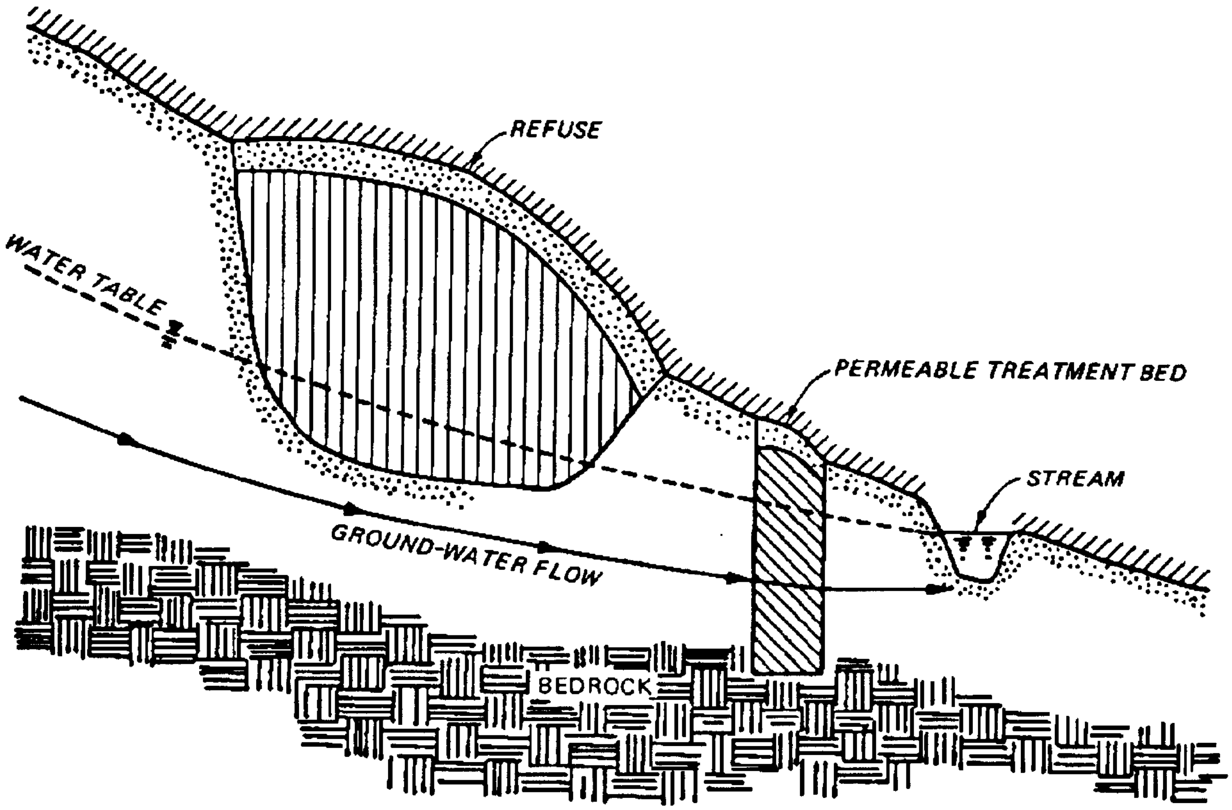


Figure 4-29. Installation of a Permeable Treatment Bed

Extrapolated bench-scale data indicate contact time needed to change 1 pH unit is 8 to 15 days.

(b) Activated carbon- -Activated carbon removes nonpolar organic contaminants such as CCl_4, PCBs, and benzene by adsorption. Activated carbon must be wetted and sieved prior to installation to ensure effective surface solution contact.

(c) Glauconitic green sand- -This sand, actually a clay, is found predominantly on the coastal plain of the Mid Atlantic states and has a good capacity for adsorbing heavy metals. Bench-scale studies indicate removal efficiencies of greater than 90 percent for As, Cu, Hg, and Ni, and 60 to 89 percent for Al, Cd, Ca, Cr, Co, Fe, Mg, Mn, and Zn, for detention times on the order of several days.

(d) Zeolites and synthetic ion exchange resins--These materials are also effective in removing solubilized heavy metals. Disadvantages such as short lifetime, high costs, and regeneration difficulties make these materials economically unattractive for use in permeable treatment beds.

c. Disadvantages.

(1) Plugging of the bed may divert contaminated ground water and channeling through the bed may occur. Both problems permit passage of untreated wastes.

(2) Changing hydraulic loads and/or contaminant levels may render the detention inadequate to achieve the design removal level.

d. Data Requirements. The principal data requirements include the contamination plume characteristics: depth to bedrock, plume cross section, leachate or ground-water velocity, and hydraulic gradient. Also the soil permeability, leachate composition, and reaction rates will have to be determined.

e. Design Criteria.

(1) A permeable treatment bed is constructed by digging a trench to an impermeable layer (bedrock or clay), filling the trench with the appropriate material, and capping to control infiltration. The width of the trench is determined by the permeability of the material used for treatment, the ground-water flow velocity, and the contact time required for treatment. These parameters are related as:

$$w_b = (v_b)(t_c) \tag{4-8}$$

where

w_b = barrier width, m

v_b = ground-water flow velocity in the barrier, m/sec

t_c = contact time to achieve the desired removal, sec

Ground-water velocity, v, in turn, is determined by Darcy*s law:

$$v = ks \tag{4-9}$$

where

s = the gradient or loss of head per unit length in the direction of flow (unitless)

k = coefficient of permeability, a soil-specific value, m/sec

(2) Since the ground-water velocity through the permeable bed cannot be predetermined, the trench should be designed for the maximum ground-water velocity through the soil. If one assumes the hydraulic gradient is equal for the soil and the permeability bed, the permeability of the barrier must equal that of the soil.

4-29. Soil Flushing.

a. Process Description. Solution mining (extraction) is the application of a solvent to a waste solid or sludge, and collection of the elutriate at well points for the removal and/or treatment of hazardous waste constituents. Typically, solvents used are water, acids (sulfuric, hydrochloric, nitric, phosphoric, carbonic), ammonia, and/or chelating agents such as EDTA which solubilize heavy metals and other inorganic ions. As the solvent is collected, a fraction can be recycled through the landfill with a make-up solution. The remainder can be treated and disposed.

b. Applications. Chemical extraction has been used by the chemical processing and mining industries for many years. The techniques are well understood, but experience with in-situ treatment of hazardous waste is lacking. Therefore, very little data are available on the application of this technology in a remedial action setting. Bench-scale laboratory studies of extraction of heavy metals from sludges and plans to conduct full-scale metal extraction from industrial wastes have been made.

c. Advantages/Disadvantages.

(1) The advantages of the process are that, if the waste is amenable to this technique and distribution, collection, and treatment costs are relatively low, solution mining can present an economical alternative to the excavation and treatment of the wastes. It may be particularly applicable if there is a high safety and health hazard associated with excavation. Also, the effectiveness and completion of the treatment process can be measured via sampling prior to wastewater treatment.

(2) Disadvantages include an uncertainty with respect to adequate contact with wastes; that is, because the wastes are buried, it is difficult to determine whether the solvent has contacted all the waste. Also, containerized waste cannot be treated effectively by this method. Another disadvantage is that the solution mining solvent or elutriate may become a pollutant itself if the system has been poorly designed.

d. Data Requirements. Principal data requirements would include laboratory testing to determine extraction efficiency of the solvents and waste analysis for presence of constituents not compatible with the solvent. Also, field testing and a geohydrologic site survey to establish potential for solvent migration into uncontaminated ground water and to establish well placement sites for collection of the elutriate are required.

e. Design Criteria. The data requirements will determine the selection of an extraction solvent, the well placement for collection of the elutriate, and the injection well locations for the extracting solvent.

4-30. Vapor Extraction.

a. Background. Soils may become contaminated in a number of ways with such volatile organic chemicals as industrial solvents and gasoline components. The sources of contamination at or near the earth*s surface include intentional disposal, leaking underground storage tanks, and accidental spills. Contamination of ground water from these sources can continue even after discharge has stopped because the unsaturated zone above a ground-water aquifer can retain a portion or all of the contaminant discharge. As rain infiltrates, chemicals elute from the contaminated soil and migrate toward ground water.

b. Process Description.

(1) A soil vapor extraction, a forced air venting, or an in situ air stripping system (Figure 4-30) revolves around the extraction of air containing volatile chemicals from unsaturated soil. Fresh air is injected or flows into the subsurface at locations around a spill site, and the vapor-laden air is withdrawn under vacuum from recovery or extraction wells.

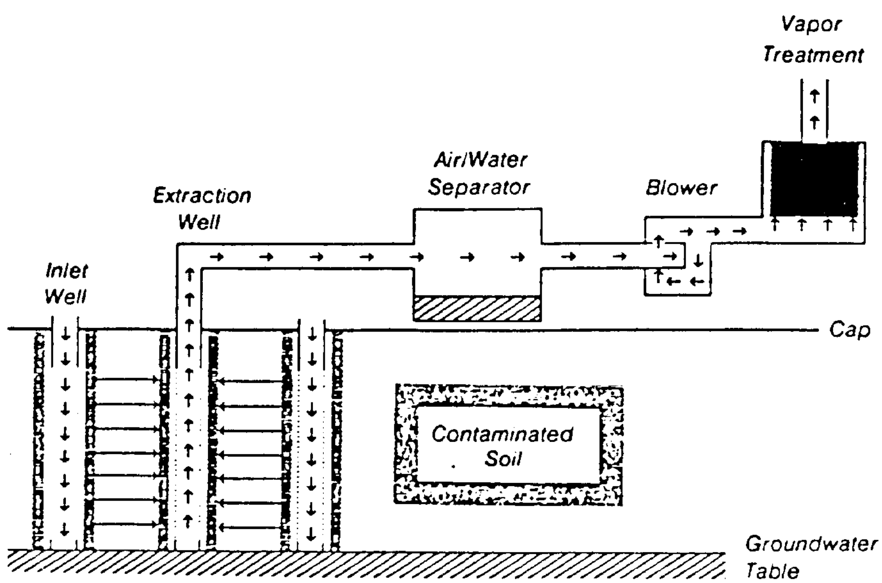


Figure 4-30. Soil Vapor Extraction System (Terravac, Inc.)

(2) In the simplest soil vapor extraction systems, air flows to an extraction well from the ground surface. To enhance air flow through zones of maximum contamination, it may be desirable to include air inlet wells in the installation. These injection wells or air vents, whose function is to control the flow of air into a contaminated zone, may be located at numerous places around the site. Typically, injection wells and air vents are constructed similarly to extraction wells. In some installations, extraction wells have been designed so they can also be used as air inlets. Usually, only a fraction of extracted air comes from air inlets. This indicates that air drawn from the surface is the predominant source of clean air.

(3) Extraction wells are typically designed to fully penetrate the unsaturated zone to the capillary fringe. Extraction wells usually consist of slotted plastic pipe placed in permeable packing and sealed near the surface to avoid “short-circuiting.” (See also paragraph 3-13 on wellpoints).

(4) During remediation, the blower is turned on and the air flow through the soil comes to an equilibrium. The flows that are finally established are a function of the equipment, the flow control devices, the geometry of well layout, the site characteristics, and the air permeability of the soil. At the end of operation, the final distribution of VOCs in the soil can be measured to ensure decontamination of the site. Wells may be aligned vertically or horizontally. Vertical alignment is typical for deeper contamination zones and for residue in radial flow patterns. If the depth of the contaminated soil or the depth to the ground-water table is less than 10 to 15 feet, it may be more practical to dig a trench across the area of contamination and install horizontal perforated piping in the trench bottom rather than to install vertical extraction wells. Usually several wells are installed at a site.

(5) The means to verify the success of cleanup is often problematic. Soil sampling is difficult to use because of the uncertainties in replicating the sampling results at a location. Measuring the soil gas concentrations are more repeatable but difficult to relate to regulatory standards, where they exist.

c. Applications. Alternatives for decontaminating unsaturated soil include excavation with onsite or offsite treatment or disposal, biological degradation, and soil flushing. Soil vapor extraction is also an accepted, cost-effective technique to remove volatile organic chemicals from contaminated soils. Soil vapor extraction can be effectively used for removing a wide range of volatile chemicals in a wide range of conditions. The design and operation of these systems is flexible enough to allow for rapid changes in operation, thus, optimizing the removal of chemicals.

d. Advantages/Disadvantages. Advantages and disadvantages of soil vapor extraction are summarized below:

Advantages	Disadvantages
Minimal disturbance of the contaminated soil	There are few guidelines for the optimal design, installation, and operation of soil vapor extraction
Systems can be constructed from standard equipment	Theoretically based design equations defining the limits of this technology are lacking and system designs are mostly empirical
Systems have been demonstrated at pilot- and field-scale	
Systems can be used to treat larger volumes of soil than are practical for excavation	Alternative designs can only be compared by the actual construction, operation, and monitoring of each design
Systems have the potential for product recovery system	

(Continued)

Advantages	Disadvantages
Spills can be cleaned up before the chemicals reach the ground water table	Vapors and condensed liquids collected from the wells may require treatment prior to discharge to the air
Systems can be integrated with other cleanup technologies to provide complete restoration of contaminated sites	Extraction of volatile chemicals from clays and silts may be difficult
Can treat soils at depths greater than in range of excavation	Determining when the site is sufficiently clean to cease operation

e. Data Requirements. A number of variables characterize the successful design and operation of a vapor extraction system:

(1) Site conditions: Distribution of VOCs, depth to ground water, infiltration rate, location of heterogeneities including paved or sealed areas, temperature, atmospheric pressure.

(2) Soil properties: Permeability, porosity, organic carbon content, soil structure, soil moisture characteristics, particle size distribution.

(3) Control variables: Air withdrawal rate, well configuration, extraction well spacing, vent well spacing, ground surface covering, inlet air VOC concentration and moisture content, pumping duration.

(4) Response variables: Pressure gradients, final distribution of VOCs, final moisture content, extracted air concentration, extracted air temperature, extracted air moisture, power usage.

(5) Chemical properties: Henry*s constant, solubility, adsorption equilibrium, diffusivity (air and water), density, viscosity.

f. Design Criteria. The design and operation of soil vapor extraction systems can be quite flexible; changes can be made during the course of operation with regard to well placement, or blower size, or air flows from individual wells. If the system is not operating effectively, changes in the well placement or capping the surface may improve it. Based on the current state of the technology of soil vapor extraction systems, the following design criteria can be recommended.

(1) Intermittent blower operation is probably more efficient in terms of removing the most chemical with the least energy.

(2) Extraction wells are usually screened from a depth of from 1.5 to 3 m (5 to 10 feet) below the surface to the ground-water table. For thick zones of unsaturated soil, maximum screen lengths of 6.1 to 9.1 m (20 to 30 feet) are specified.

(3) Air/water separators are simple to construct and should probably be installed in every system.

(4) Installation of a cap over the area to be vented reduces the chance of extracting water and extends the path that air follows from the ground surface, thereby increasing the volume of soil treated.

(5) Incremental installation of wells, although probably more expensive, allows for a greater degree of freedom in design. Modular construction where the most contaminated zones are vented first is preferable.

(6) Use of soil vapor probes in conjunction with soil borings to assess final cleanup is less expensive than use of soil borings alone. Usually a complete materials balance on a given site is impossible because most sites have an unknown amount of VOC in the soil and in the ground water.

(7) Soil vapor extraction systems are usually only part of a site remediation system.

(8) Although a number of variables intuitively affect the rate of chemical extraction, no extensive study to correlate variables to extraction rates has been identified.

(9) Well spacing is usually based on some estimate of the radius of influence of an individual extraction well. Well spacing has ranged from 15 to 100 feet. Well spacing should be decreased as soil bulk density increases or the porosity of the soil decreases. One of the major differences noted between systems was the soil boring diameter. Larger borings are preferred to minimize extracting liquid water from the soil.

(10) Wells should be constructed with approximately 20 feet of blank casings between the top of the screen and the soil surface to prevent the short circuiting of air and to aid in the extraction of deep contamination.

(11) Initial VOC recovery rates are relatively high, then decrease asymptotically to zero with time. Several studies have indicated that intermittent venting from individual wells is probably more efficient in terms of mass of VOC extracted per unit of energy expended. This is especially true when extracting from soils where mass transfer is limited by diffusion out of immobile water.

(12) Optimal operation of a soil vapor extraction system may involve taking individual wells in and out of service to allow time for liquid diffusion and to change air flow patterns in the region being vented.

(13) Air injection has the advantage of controlling air movement, but injection systems need to be carefully designed.